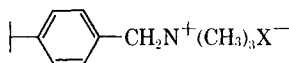


Preparation and Properties of a Neophyl Type Anion Exchange Resin

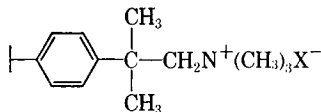
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Synopsis

The common strongly basic Type I anion exchange resins,



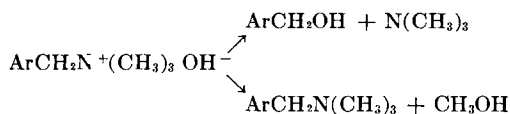
contain benzylictrimethylammonium groups. In OH^- form, the resins are unstable above 60°C . due to nucleophilic attack by OH^- on the benzylic and methyl carbon atoms. Reactivity of benzylic carbon sites relative to methyl sites is about 4 to 1. More stable resins would be desirable, so laboratory synthesis and stability study was made of a resin which contained neither benzylic carbon atoms nor β -carbon atoms having hydrogen atoms which could give elimination reactions. This resin,



containing neophyltrimethylammonium groups, nevertheless lost strong base capacity more readily than a comparative resin containing benzylic trimethylammonium groups. The breakdown was primarily at the methyl carbon atoms, however, so almost all weak base capacity was retained. The greater reactivity of methyl groups on the neophyl resin—relative to methyl groups on benzylic resin—can be due to internal compressional strain between the methyl groups of the nitrogen and the methyl groups of the β -carbons.

INTRODUCTION

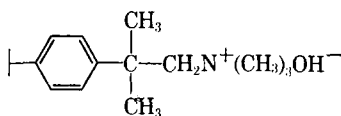
The chemical stability of Type I strongly basic anion exchange resins is somewhat low. For example, the resins in the hydroxide form are not suitable for water treatment operation at temperatures above 60°C .¹ Breakdown can occur by nucleophilic attack by OH^- ion (S_N2 attack) on the benzylic or methyl carbon atoms, which leads to either loss in total capacity or loss in strong base capacity.



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Statistically, one expects that 25% of the breakdown would occur at the benzylic carbon atom if each of the carbon sites attacked were equally reactive. Actually, however, the electronic effects of the aryl ring enhance the reactivity at the benzylic carbon atom, and about 60% of the breakdown occurs there.^{1,2} The benzylic site thus is about four times as reactive as a single methyl site.

One possible way to improve the stability of the hydroxide form resin then would be to insulate from the aryl ring the benzylic carbon atom which is attached directly to the quaternary nitrogen atom. Inserting another $-\text{CH}_2-$ group between the nitrogen and the aryl ring gives a structure which would undergo readily the Hofmann elimination reaction to produce a vinyl group attached to the aryl ring. However, insertion of a $-\text{C}(\text{CH}_3)_2-$ group would give a neophyl quaternary amine structure,



which would have no eliminatable hydrogen atoms on the carbon atoms which are β to the nitrogen. Displacement reactions at the $-\text{CH}_2-$ group next to the nitrogen should be very slow due to steric hindrance. Would a resin of this structure then be more stable in the OH^- form than the conventional benzylic Type I resins? Laboratory preparation and testing of a resin of this neophyl type was undertaken in order to answer that question.

EXPERIMENTAL SYNTHESIS OF MONOMERS AND POLYMERIZATION TO RESINS

Vinylbenzyl Cyanide

An oily *ortho-para* mixture of vinylbenzyl cyanide isomers (about $1/3$ *ortho*), prepared from vinylbenzyl chloride isomers³ plus NaCN ⁴ by J. R. Runyon of The Dow Chemical Company, Midland, Michigan, was used.

ANAL. Calcd. for $\text{C}_{10}\text{H}_9\text{N}$: C, 83.85%; H, 6.34%; N, 9.78%. Found: C, 83.72%; H, 6.32%; N, 9.68%.

Vinyl- α,α -dimethylbenzyl Cyanide

A mixture of vinylbenzyl cyanide (43 g., 0.3 mole) and dry ether (200 ml.) was added with stirring to a suspension of NaH (16 g., 0.67 mole) in ether (100 ml.). The mixture was heated at reflux for 3 hr.; then a solution of CH_3I (93 g., 0.6 mole) in ether (100 ml.) was added over a period of 40 min. The mixture was heated at reflux for 3 hr. and allowed to stand at room temperature for another 16 hrs. Ethanol (25 ml.) was added to decompose the excess NaH . Water (200 ml.) was added and the mixture was neutralized with acetic acid. The ether layer was separated, the aqueous layer

was extracted with more ether and the combined ether solutions were dried with Na_2SO_4 and concentrated to yield a viscous oil (43 g.), whose infrared spectrum indicated that dimethylation was about 60% complete.⁵ The oil was methylated again by the above procedure to yield product oil whose dimethylation was 90% complete.

Vinyl Neophyl Amine

A solution of the above cyanide (41 g., 0.26 mole) in dry ether (300 ml.) was added over a period of 45 minutes to a stirred suspension of LiAlH_4 (7.9 g., 0.26 mole) in ether (500 ml.). After another 3 hr., water (100 ml.) was added carefully to decompose excess LiAlH_4 ; then enough NaOH solution to dissolve precipitated $\text{Al}(\text{OH})_3$ was added. The ether layer was separated, the water layer was washed with ether, and the combined ether layers were dried with Na_2SO_4 . Concentration yielded crude vinyl neophyl amine as a viscous oil (30 g.). The amine was purified by dissolving it in aqueous HCl , washing the solution with ether, and reprecipitating the amine with NaOH solution. The product amine (25 g.) then contained only traces of the corresponding imine, according to infrared data.⁵

Vinyl Neophyl Trimethylammonium Iodide

A solution of vinyl neophyl amine (25 g., 0.14 mole) and CH_3I (61 g., 0.143 mole) in ethanol (250 ml.) was added with stirring to NaOH pellets (17 g., 0.43 mole). After the initial exothermic reaction had subsided the mixture was allowed to cool to room temperature. More CH_3I and NaOH were added in small portions (20 and 10 g., respectively) until the reaction no longer was exothermic at each addition. The reaction mixture was neutralized with glacial acetic acid, filtered, and the filtrate concentrated and refiltered. Solid so obtained was vinyl neophyl trimethylammonium iodide. Some vinyl neophyl dimethylamine also was obtained, which was treated with CH_3I to yield more vinyl neophyl trimethylammonium iodide (total of 40 g.).

ANAL. Calcd. for $\text{C}_{15}\text{H}_{24}\text{NI}$: C, 52.17%; H, 6.96%. Found: C, 52.18%; H, 6.73%.

Vinyl Neophyl Trimethylammonium Chloride

The above iodide (35 g., 0.1 mole) was converted to the chloride by refluxing it for 1 hr. in methanol with two successive portions of AgCl (21 g., 0.2 mole). The solution was filtered and the solvent was removed from the filtrate in vacuo, by using a rotary evaporator, to yield vinyl neophyl trimethylammonium chloride as a very viscous glass.

Polymerizations to Form Neophyl Type Ion Exchange Resins

Mixtures of 10 parts of vinyl neophyl trimethylammonium chloride, 1–2 parts of 50% divinylbenzene, 10 parts of methanol, 1 part of 10% *tert*-butyl hydroperoxide in methanol, and 0.1 part of ethylenediaminetetraacetic acid were degassed and sealed in vacuo in small glass bombs. Heating

the homogeneous mixtures at 60°C. for 20 hr. yielded flexible rods of cross-linked copolymers which were subdivided, washed with water and methanol to leach out any unreacted monomers, and screened to 10–40 mesh in the water-swollen condition. Subdivided resins were produced which contained 5, 7.5, and 10% divinylbenzene crosslinking (nominal values, based on amount of divinylbenzene charged). These are resin numbers 1, 2, and 3 of Table I.

Polymerizations to Form Special Type I Ion Exchange Resins

For comparison stability tests, special laboratory preparations of benzylic Type I resins were made by a procedure similar to that immediately above, using a glassy concentrate of *ortho* and *para* mixture of vinylbenzyl trimethylammonium chloride (about $\frac{1}{3}$ *ortho*) and divinylbenzene. The quaternary monomer was prepared by reacting vinylbenzyl chloride with trimethylamine.^{6,7} Nominal divinylbenzene crosslinkings of the preparations were 7.5 and 10% (resin numbers 4 and 5 of Table I).

Commercial Type I Ion Exchange Resin

A sample of conventional Type I anion exchange resin, DOWEX 1 of 7.5% crosslinking, was obtained from The Dow Chemical Company, Midland, Michigan.

EXPERIMENTAL DETERMINATION OF STABILITIES OF RESINS

The resins in the completely water-swollen chloride forms were centrifuged and water contents were found by the loss of weight on drying small samples. The water contents of the special Type I resins were somewhat higher than those of the neophyl type resins of the same nominal crosslinking, and all values were much higher than the water content of the commercial Type I resin (see Table I). The neophyl monomer, which had no chain transfer tendencies which might be associated with benzylic hydrogens, and whose charged nitrogen atom was far removed from the aryl ring, apparently copolymerized with the divinylbenzene more effectively than did the vinylbenzyl trimethylammonium chloride monomer. This would explain the somewhat lower water contents of the neophyl resins. The much lower water content of the commercial Type I resin probably was due mainly to the fact such resin is made by chemically modifying styrene and divinylbenzene copolymers which are prepared without the need or use of compatibilizing solvents such as the methanol required with the quaternary chloride monomers. Consequently, the retractile forces on the water-swollen polymer network of the commercial resin operate from a nonswollen base, rather than from about a 50% swollen base.

Fresh resin samples (about 10 ml.) in 0.5 in. diameter glass columns were washed with chloride-free 1N NaOH solution until eluate samples gave no chloride indication with AgNO₃ solution. The resins then were washed with water until the eluate tested neutral. The resins were backwashed and wet settled, and their volumes were compared with the wet settled

TABLE I

	Neophyl resins (lab. preparations)			Special Type I (laboratory preparations)		Regular Dowex 1 (com- mercial)
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
A. Crosslinking (DVB), %	5	7.5	10	7.5	10	7.5
B. Water content (Cl ⁻ form), %	83	78	68	88	87	48
C. Volume increase of OH ⁻ over volume of Cl ⁻ form, %	21	29	22	53	53	7
D. Initial strong base capacity, meq./ml.	3.3	2.9	3.2	4.4	4.3	3.4
E. Strong base capacity after 31 days in OH ⁻ form at 100°C., meq./ml.	2.1	2.2	2.7	3.7	3.6	2.0
F. Loss of strong base capacity after 31 days, %	33	24	16	16	16	41
G. Strong base capacity after 7 days more in 5 <i>N</i> NaOH at 100°C., meq./ml.	1.1	1.3	0.9	3.1	2.8	1.4
H. Final overall loss of strong base capacity, %	67	55	72	30	35	59
I. Initial total base capacity, meq./ml.	3.5	3.8	4.2	4.5	4.2	3.4
J. Total base capacity after 31 days in OH ⁻ form at 100°C., meq./ml.	3.5	3.7	4.0	4.2	4.0	2.7
K. Loss of total base capacity after 31 days, %	0	3	5	7	5	20
L. Total base capacity after 7 days more in 5 <i>N</i> NaOH at 100°C., meq./ml.	3.3	3.6	3.7	3.7	3.4	2.1
M. Final overall loss of total base capacity, %	6	5	12	18	14	38
N. Fraction of overall per cent loss of strong base capacity which was accompanied by gain of weak base capacity	0.9	0.9	0.8	0.4	0.5	0.4

volumes of the resins in the chloride form (see Table I). Because of the high deformability and the irregular size and shape of the prepared resins, the volume measurements were not highly accurate. However, as would be expected from the water contents of the various resins, the commercial Type I resin swelled far less in going from the chloride to the hydroxide form than did the other resins (less than 10%), and the neophyl type resin swelled less than the special benzylic Type I resin (about 25% compared to about 50%).

The strongly basic capacities of the resins (salt-splitting capacities) were found by washing the resins with 1*N* NaCl solution until the eluate samples tested neutral, and titrating the total eluate fractions with acid. The total anion exchange capacities of the resins (strongly basic plus weakly

basic capacities) were obtained after first rinsing the resins with about 10 bed volumes of 1*N* HCl, and washing out excess HCl with methanol until no further Cl⁻ ion was present in the wash samples. The resins then were eluted with an aqueous solution, 0.5*N* in HNO₃ and 0.15*N* in NaNO₃, until samples of the eluate tested chloride-free to AgNO₃, and the total eluate was analyzed for chloride content. To return the resins completely to the OH⁻ form, they were washed with about 400 bed volumes of 0.5*N* Na₂SO₄ solution and then with 2*N* NaOH until eluate samples no longer gave precipitate with Ba(OH)₂ solution. Water rinsing then removed excess NaOH.

Simple static tests gave the comparative stabilities of the resins in the OH⁻ form. The resin samples in pure water were heated in sealed glass tubes for 30 days at 100°C. The total capacities and the strongly basic capacities then were determined as described before. Further data on stabilities then were obtained by similar heating of the analyzed resin samples, reconverted to OH⁻ forms, in 5*N* NaOH for another 7 days. Table I summarizes results.

DISCUSSION OF RESULTS

Examination of Table I shows that, contrary to hopes, the heated quaternary neophyl type resins were not even as stable as the benzylic resins in their ability to retain strongly basic capacity (rows E and G). Neophyl resins lost about two-thirds of their strong base capacity during the total tests. The benzylic Type I resins made by analogous laboratory preparations lost only about one-third of their strongly basic capacity during these same testing conditions, although the commercial Type I resin lost close to two-thirds of its strongly basic capacity. The special benzylic Type I resins made by laboratory preparations constitute the best models for comparison of the stability of the neophyl type resins. They were made by similar methods, and their water contents are much more similar to those of the neophyl resins than are the lower water contents of the commercial Type I resin. The high water contents of the special benzylic Type I resins mean that these resins have much larger swollen volumes per equivalent of ArCH₂N⁺(CH₃)₃ groups and OH⁻ ions. Consequently the rate of breakdown is much less than that of the commercial Type I resin, since the time required to complete a definite fraction of an S_N2 reaction is inversely proportional to the initial concentration of reactants.

The neophyl resins, on the other hand, did retain their total base capacity far better than did the benzylic resins (see rows K, M, N of Table I). Only about 1/12 of the capacity was lost in the overall test with the neophyl resins, compared to about 1/6 and about 1/3 of the capacities with the special and commercial Type I resins. Insertion of the —C(CH₃)₂— group into the usual resin structure almost stopped all breakdown at the —CH₂— group next to the nitrogen, as was expected. But the presence of the —C(CH₃)₂— group somehow caused the CH₃— groups on the nitrogen to become more susceptible to S_N2 attack by OH⁻ ion. The results cor-

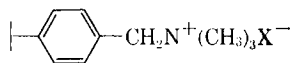
relate with the observations of earlier workers that benzyltrimethylammonium hydroxide decomposed mainly to benzyl alcohol and trimethylamine, and that neopentyl trimethylammonium hydroxide decomposed completely to neopentyl dimethylamine and methyl alcohol.^{8,9} No relative rates of decomposition were given. However, the present finding that the methyl groups of the neophyl type resins are more susceptible to attack by OH⁻ ion than the methyl groups of the benzylic type resins requires explanation. The explanation may be internal steric strain between the methyl groups of the bulky —C(CH₃)₂— group and the methyl groups on the quaternary nitrogen. Such strain could weaken the CH₃-N⁺ \leq bond considerably, and Brown and Bonner have reported such strain is present in the related neopentyl trimethylammonium ion.¹⁰

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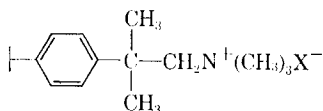
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Résumé

Les résines échangeuses d'anions du type I extrêmement basiques



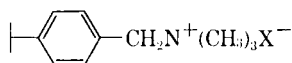
contiennent les groupes ammonium triméthyle benzyliques. Dans la forme OH⁻, les résines sont instables au-dessus de 60°C par suite de l'attaque nucléophile par OH⁻ sur les carbones benzyliques et méthyliques. La réactivité au niveau du carbone benzylique relativement au carbone méthylique est d'environ 4 à 1. Des résines plus stables seraient souhaitées; ainsi la synthèse au laboratoire et l'étude de la stabilité pourraient se faire sur une résine ne contenant pas d'atome de carbone benzylique, ni d'atome de carbone- β porteurs d'atomes d'hydrogène qui pourraient donner des réactions d'élimination. Cette résine



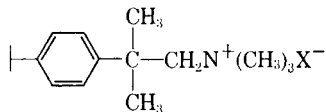
contenant des groupes ammonium triméthyl néophylique, perdrait néanmoins plus rapidement sa capacité de base forte qu'une résine comparative contenant les groupes ammonium triméthyl-benzylique. La cassure s'effectue tout d'abord aux atomes de carbone méthylique; cependant, quasi toute la capacité de base faible est retenue. La plus grande réactivité des groupes méthyles dans les résines néophyliques relativement aux groupes méthyliques dans les résines benzyliques, peut être due à la tension de compression interne entre les groupes méthyliques et l'azote et les groupes méthyliques des-carbones- β .

Zusammenfassung

Die üblichen stark basischen Anionenaustauscherharze vom Typ I,



enthalten Benzyl-Trimethylammoniumgruppen. In der OH^- -Form sind die Harze oberhalb 60°C infolge des nukleophilen Angriffs von OH^- auf die Benzyl- und Methylkohlenstoffatome instabil. Die Reaktivität der Benzylkohlenstoffe relativ zum Methyl beträgt etwa 4 zu 1. Da stabilere Harze wünschenswert sind, wurde eine Synthese- und Stabilitätsuntersuchung im Laboratorium an einem Harz ohne Benzylkohlenstoffatome oder β -Kohlenstoffatome mit Wasserstoffatomen, die zu Eliminierungsreaktionen führen könnten, gemacht. Dieses Harz,



das Neophyl-Trimethylammoniumgruppen enthält, verliert nichtsdestoweniger die starke basische Kapazität leichter als ein vergleichbares Harz mit Benzyl-Trimethylammoniumgruppen. Der Rückgang erfolgte primär an den Methylkohlenstoffatomen sodass fast die ganze schwach basische Kapazität erhalten blieb. Die grössere Reaktivität der Methylgruppen am Neophylharz—im Vergleich zu den Methylgruppen am Benzylharz—kann auf innere Kompressionsspannungen zwischen den Methylgruppen des Stickstoffs und den Methylgruppen des β -Kohlenstoffs zurückzuführen sein.

Received November 21, 1963