REARRANGEMENT OF POLY[(4-VINYLBENZYL)DIMETHYLAMINE OXIDE] TO POLY[O(4-VINYL BENZYL)-N,N-DIMETHYL HYDROXYLAMINE]

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Tertiary nitrogen of weakly basic anion-exchange resins of the type of poly[(4-vinylbenzyl)dimethyl-amine] was oxidised and amine oxide formed was rearranged to give poly[O(4-vinylbenzyl)-N-N-di-methylhydroxylamine]. The reaction was followed by measuring the selectivity variation of the anion-exchange resin towards Cl$^-$ ions and also by comparing IR spectra of the polymers with low-molecular-weight model compounds.

Weakly basic anion-exchange resin of the type of poly[(4-vinylbenzyl)dimethylamine] exhibit very high stability. Their lifetime is practically unlimited from the point of view of the chemical stability of the functional group under operating conditions of a conventional ion-exchange process in water at the temperatures up to 100°C. However, if the anion-exchange resin is exposed to un-usual conditions, *e.g.* higher temperature, oxidising agents, certain chemical changes of functional groups, which can be deduced from reactions of benzyldimethylamine, can take place.

From the literature it is known that tertiary amines can be easily transformed to amine oxides, *e.g.* by reacting it with hydrogen peroxide[1,2], and that these amine oxides can be rearranged to N,N,O-trialkylhydroxylamines. In the present work we have concerned ourselves with a polymeranalogous reaction of oxidation and rearrangement, using weakly basic anion-exchange resin of the type of poly[(4-vinyl-benzyl)dimethylamine].

EXPERIMENTAL

I.R. spectra of low-molecular-weight models and the corresponding polymers were run on a Perkin-Elmer 621 apparatus in the range of 4 000—200 cm^{-1}. Liquid model compounds were measured in a cell 0·025 mm thick. KBr-disc technique and grinding in liquid nitrogen[3] were used for measuring polymers; KBr-discs, prior to measurements, were dried over P_2O_5 at 10 Torr overnight.

Model compounds. Twice rectified benzyldimethylamine, b.p. 67°C/15 Torr, was used. Benzyl-dimethylaminoxide was prepared according to Cope and Towle[2]; solid oxide was dried to constant weight over P_2O_5 at 100°C/7 Torr. O-Benzyl-N,N-dimethylhydroxylamine was prepared ac-cording to (ref.[2]), b.p. 60—70/7 Torr, n_D^{25} 1·4948.

Ion-Exchange Resins Used

Anion-exchange resin S4-DM is a gel, standard type of weakly basic anion-exchange resin prepared from styrene–divinylbenzene (4%) copolymer which was chloromethylated with monochlordimethyl ether in the presence of ferric chloride catalyst and aminated with dimethylamine; it is in the form of yellowish, transparent spheres having the diameter of 0·3—0·8 mm. Anion-exchange resin Ns—DM is a macroporous type of weakly basic anion-exchange resin prepared from macroporous styrene–divinylbenzene (10%) copolymer which was copolymerised in the presence of pentane, then chloromethylated and aminated with dimethylamine; it is in the form of white, nontransparent beads; the particle diameter being 0·3—1·2 mm.

Anion-exchange resins were transformed to OH-form by washing with 4% solution of sodium hydroxide, and by a subsequent washing with sodium chloride solution strongly basic groups were transformed to Cl-form and then the resins were washed with demineralised water (samples *Ia* and *IIa*).

Properties of anion-exchange resins in the OH-form: water content in fully swollen state (%): *Ia* 40·0, *IIa* 41·1; Swelling capacity (g of water/g of dry resin): *Ia* 0·835, *IIa* 0·860; ion-exchange capacity, weakly basic (meq/cm^3): *Ia* 1·33, *IIa* 1·27; ion-exchange capacity, strongly basic (meq/cm^3): *Ia* 0·37, *IIa* 0·28.

Oxidation of anion-exchange resins. To the samples of anion-exchange resins 17·8 g of dry residue in OH-form (strongly basic groups were in Cl-form) was added 37 g of 30% hydrogen peroxide and 16·5 g of deionised water (molar ratio of functional groups and of H_2O_2 was 1/3) and the mixture was stirred for 24 hours at 20—25°C. Then the anion-exchange resins were washed with deionised water untill the eluates were free of hydrogen peroxide (iodometric test) and then they were filtered off (samples *Ib* and *IIb*).

Rearrangement of amine oxides of anion-exchange resins. Oxidised anion-exchange resins were, after drying to constant weight (over P_2O_5 at 20—25°C/20 Torr), heated (10 g) in toluene suspension at 110°C for 8 hours. After washing with ethanol, the resins were dried for 6 hours at 150°C (samples *Ic* and *IIc*).

Ion-exchange equilibrium OH^-/Cl^-. The resin sample (1 g) was placed into a bulb with a ground-in stopper and then 0·05M hydrochloric acid was added and the contents were from time to time shaken. The Cl^- concentration was determined by potentiometry.

RESULTS AND DISCUSSION

Polymeranalogous reactions with an insoluble polymer have the advantage over the classic syntheses with monomolecular compounds, that the separation of reaction products is easy and simple. But on the other hand, the disadvantage of this process is, that the resulting polymer contains all functional groups according to suggested synthesis. Therefore, the identification of reaction products and the determination of the conversion is more complicated and more difficult.

The oxidation and the rearrangement of amine oxide to hydroxylamine derivative in the case of dimethylaminated cross-linked poly(styrene-co-divinylbenzene), *i.e.* the gel anion-exchange resin (*I*) and the macroporous anion-exchange resin (*II*), was checked by determining the nitrogen content, by comparing equilibrium state of the exchange of OH^- and Cl^- ions and by comparing IR spectra of model compounds with polymers.

TABLE I

Infrared Spectra ($\bar{v}$, cm^{-1}) of Benzyl Derivatives of Dimethylamine, Dimethylamine Oxide and N,N-Dimethylhydroxylamine and Their Polymeranalogues (anion-exchange resins)

Relative intensities of absorption bands: s strong, m medium, w weak, sh shoulder.

Derivative of dimethylamine		Dimethylamine oxide		N,N-Dimethylhydroxyl-amine	
model	polymer	model	polymer	model	polymer
—	3 412 s	3 437 s	3 420 s	—	3 412 s
3 086 m	3 079 w	—	—	3 084 m	3 082 w
3 062 m	3 043 m	—	—	3 059 m	3 049 sh
3 030 m	3 019 m	3 021 m	3 021 m	3 028 s	3 022 m
2 977 m	2 970 m	—	—	2 984 s	2 988 w
2 942 s	—	2 955 m	—	2 952 s	—
—	2 922 s	—	2 929 s	—	2 922 s
2 906 s	—	—	—	2 896 s	—
2 857 s	2 852 s	2 852 w	2 852 w	2 851 s	2 852 s
2 816 s	2 811 s	—	—	2 811	2 812 m
2 772 s	2 766 s	—	—	2 773 sh	2 773 m
—	—	—	—	2 764 m	2 764 m
—	2 722 w	—	—	—	—
2 702 w	2 692 sh	—	—	—	—
1 947 m	—	—	—	1 944 m	—
1 871 m	—	—	—	1 869 m	—
1 806 m	—	—	—	1 801 m	—
1 750 m	—	—	—	1 743 w	—
1 705 m	—	—	—	1 705 m	1 701 m
1 695 m	—	1 696 m	1 694 sh	—	—
—	1 643 m	1 647 m	1 637 m	—	—
1 603 m	1 613 m	1 598 w	1 607 m	1 601 m	1 603 m
—	1 596 m	—	—	—	—
1 583 m	1 589 sh	—	—	1 581 m	1 573 w
1 494 s	1 513 m	1 494 m	1 505 m	1 491 s	1 510 m
—	—	—	—	—	1 490 m
1 462 sh	1 486 w	1 455 m	1 466 s	1 462 s	1 464 s
1 452 s	1 454 s	1 437 sh	1 444 s	1 448 sh	1 450 s
—	1 377 sh	1 385 w	1 381 w	—	1 380 m
1 359 s	1 362 s	1 375 w	1 377 m	1·355 s	1 359 m
1 310 m	1 314 m	1 296 w	—	1 301 m	1 302 w
1 256 s	1 258 s	1 270 w	1 250 w	1 250 w	1 250 m
1 200 w	1 211 w	1 211 m	1 210 m	1 198 s	1 204 m
—	—	1 194 m	1 183 m	—	—
1 170 s	1 164 s	—	—	1 157 m	1 164 s
1 140 s	1 137 m	—	—	—	—
1 093 m	1 100 m	—	1 113 w	—	1 100 w

TABLE I
(Continued)

Derivative of dimethylamine		Dimethylamine oxide		N,N-Dimethylhydroxyl-amine	
model	polymer	model	polymer	model	polymer
—	1 090 m	—	—	—	—
1 072 m	—	1 076 m	—	1 071 m	—
1 041 s	—	—	—	—	—
1 031 s	1 031 sh	—	—	—	—
1 020 s	1 022 sh	1 026 w	—	1 021 s	1 025 s
—	1 011 s	1 001 m	1 011 w	—	—
—	—	—	994 m	991 m	991 sh
972 m	970 m	972 w	965 w	972 w	—
—	936 w	929 m	922 m	—	—
904 m	912 w	901 m	899 w	901 s	883 w
847 s	850 s	831 s	842 s	842 s	851 s
—	—	—	—	810 w	811 s
—	—	—	—	798 w	—
—	—	—	—	781 m	—
—	752 m	771 m	760 m	764 s	760 m
733 s	729 s	—	—	730 s	—
696 s	693 s	691 s	691 s	689 s	695 s

Nitrogen content in copolymers, which were originally in OH-form (Ia, IIa), was after oxidation (Ib, IIb) and rearrangement (Ic, IIc) practically identical.

Sample:	Ia	Ib	Ic	IIa	IIb	IIc
N, %:	5·35	4·83	4·97	5·10	4·98	5·03

Therefore, the different values of weight-exchange capacities (meq/g) of original anion-exchange resins and their products of oxidation and rearrangement should be due to the change of the character of the functional group:

Resin:	Ia	Ib	Ic	IIa	IIb	IIc
Capacity, weakly basic:	3·19	2·65	2·15	3·22	2·73	1·71
Capacity, strongly basic:	1·07	0·93	0·47	0·78	0·80	0·59

From the literature it is known that amine oxides are markedly weaker bases than corresponding tertiary amines[4]. Still more weaker base would be the hydroxylamine

derivative after disappearing of the semipolar bond by rearrangement and also because of the neighbourhood of the more electronegative oxygen and functional nitrogen. Therefore, the method used for the determination of ion-exchange capacity must give us lower values because hydrochlorides, obtained after polymeranalogous reactions, would undergo hydrolysis more easily. These results are in good agreement with equilibrium state of the exchange of OH^- and Cl^- ions in dependence on the overall amount of Cl^- ions in the system at their constant initial concentration in the water phase (Fig. 1).

The data of IR spectra of low molecular compounds and corresponding gel resins are summarised in Table I. (The spectra of macroporous resins are identical with the spectra of gel products and, therefore, are not included in the table.) The spectra of polymer products, in contrast to low-molecular-weight products, exhibit less sharp absorption bands and wave-number shifts, which are in most cases in the range of $0-20$ cm^{-1}. The polymer products, in contrast to model compounds, have in their IR spectra, with the exclusion of O-benzyl-N,N-dimethylamine oxide, a broad absorption band at 3400 cm^{-1}, which we assign to sorbed water[5,6] which is not removable even by an intensive drying.

The absorption band in the range of $3019-3030$ cm^{-1}, which have all compounds measured, we assign to stretching C—H vibration of the aromatic ring[7,8]. The bands at $2852-2955$ cm^{-1} of all compounds can be ascribed to stretching vibration of CH_2 group: the symmetric stretching vibration of CH_2 group of all measured samples is seen at $2851-2857$ cm^{-1} (ref.[9]). Antisymmetric stretching vibration band of polymers is at $2922-2929$ cm^{-1} (ref.[9]), while this band of low-molecular-weight models is shifted to $2942-2955$ cm^{-1}.
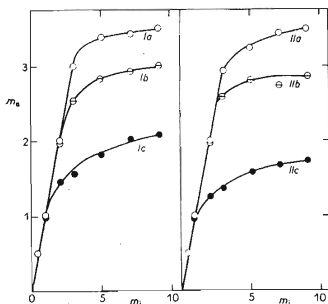

Fig. 1

Relation Between Added (m_i) and Absorbed (m_a) Amount of Hydrogen Chloride (mequiv.) per 1 g of Standard (*I*) and Macroporous (*II*) Anion-Exchange Resin

Anion-exchange resins: *Ia, IIa* original, *Ib, IIb* after oxidation, *Ic, IIc* after rearrangement.

The bands in the range of $2970-2988$ cm^{-1} in the spectra of derivatives of dimethylamine and hydroxylamine, we ascribe to asymmetric stretching vibration of C—N bond in N—CH$_3$ group[10]. The corresponding symmetric vibrations of the same derivatives were found[10] at $2764-2772$ cm^{-1}; in the case of hydroxylamine a doublet is observed.

The region of $1650-2000$ cm^{-1}, which is characteristic for aromatic substitution[8], is prominent in the spectra of benzyldimethylamine and O-benzyl-N,N-dimethylhydroxylamine, while in the spectra of the polymers and benzyldimethylamine oxide is suppressed (low-molecular-weight model compounds have monosubstituted aromatic ring, while the analogous polymers are disubstituted). In the 1490 to 1613 cm^{-1} region all compounds measured have at least two bands, which can be attributed to C=C in-plane vibration of the aromatic ring[7]. The $1355-1385$ cm^{-1} region is most probably specific for deformation vibration of dimethyl group[5,8].

In the $1157-1170$ cm^{-1} region there are observed absorption bands only in the case of dimethylamine derivatives and of N,N-dimethylhydroxylamine, which can be assigned to deformation vibration of N—CH$_3$ group[10]. To the deformation vibrations of mono- and disubstituted aromatic ring can be assigned the bands found in the $1001-1176$, $803-851$ and $729-771$ cm^{-1} regions (refs[7-9]). Deformation vibration, specific for monosubstituted aromatic ring, of the compounds measured is in the $689-696$ cm^{-1} region. In the case of low-molecular-weight models the absorption bands at $1071-1076$ and $729-733$ cm^{-1} can be, with certainty, assigned to deformation vibration of monosubstituted aromatic ring.

From the comparison of model compounds and corresponding polymers it follows (Table I) that the spectra of dimethylamine derivatives and N,N-dimethylhydroxylamine are very similar, while the spectra of amine oxide derivative differ from them considerably. We have found two regions characteristic for amine oxide, in these regions absorb both derivatives of amine oxide and do not absorb other compounds. It is in the $922-929$ cm^{-1} and $1183-1194$ cm^{-1} regions. We do not take into consideration a weak band at 936 cm^{-1} appearing at polymer derivative of dimethylamine. Giguere and Chin[11] have found for trimethylamine oxide an intensive band at 937 cm^{-1} which they assign to stretching vibration of C—N bond. Mathias-Noël and coworkers[12] quote for N—O bond in tertiary amine oxides the $950-970$ cm^{-1} region. On the other hand, Wiley and Slymaher[13] assign to N—O bond in N-oxides of pyrimidines and pyridines the $1255-1300$ cm^{-1} region. It seems that the position of N—O bond in the spectrum of amine oxides is considerably dependent on the structural neighbourhood of this bond in a given compound. Therefore, we think that the bands specific for amine oxides in the series of studied compounds do not exclude the possibility to assign them either to N—O or to C—N bond. From Table I if follows, that low-molecular-weight model and its analogous polymer have, from the viewpoint of IR spectra, very similar behaviour. While the spectra of dimethylamine and N,N-dimethylhydroxylamine are similar, the spectra of derivatives of di-

methylamine oxide considerably differ from the first two ones. These facts, in connection with the sequence of reactions which were performed on the polymer anion-exchange resins, lead us to the conclusion that the IR spectra of prepared polymer-analogues are in agreement with supposed reactions.

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