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1957

SovietRxiv

Abstract

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CHEMISTRY

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ON THE AMINATION OF CHLORINATED RUBBER

(Presented by Academician I. N. Nazarov on 16 X 1956)

In 1951 a patent was issued for the amination of chlorinated rubber (⁀1). Upon heating for three hours in an autoclave a 20% solution of chlorinated rubber (64% Cl) with an equal amount of ammonia and a small amount of a sulfonated product as emulsifier, the authors obtained a brown mass containing 4.1% N_2 and 27% Cl and insoluble in solvents for rubber. One kg of this mass absorbs 118.8 g of HCl from 1 *n* hydrochloric acid and 10.3 g of HCl from 0.001 *n* hydrochloric acid. In 1952 one of the authors of the method (⁀2) took out a patent on another method for preparing aminochlorinated rubber. By treating a 20% dioxane solution of hydrochlorinated rubber (16–18% Cl) or chlorinated rubber (62–64% Cl) with an excess of ammonia or ethylenediamine at 90° for 1–2 hours, he obtained a product also possessing anion-exchange properties. When used as a filler for rubber, the product accelerates vulcanization and improves the properties of rubber with respect to oxidizability, abrasion, oil resistance, and adhesion of the vulcanizate to cellulose derivatives.

The products of amination of chlorinated rubber may find important fields of application, the most interesting of which is the use of their ion-exchange properties. However, a satisfactory solution to the problem of obtaining aminochlorinated rubber with properties meeting the requirements of ion-exchange practice is possible only on the basis of more systematic investigations of the processes of amination of chlorinated rubber. In the literature we have been unable to find any data on this question. The aim of the present work is to initiate such investigations.

The amination of chlorinated rubber may be assigned to the reactions involving the conversion of linear high-molecular compounds into plane-spatial ones by polycondensation with di- and polyfunctional low-molecular substances. The composition, structure, and the ion-exchange properties of the amination product determined by them are undoubtedly in a very complex dependence on a number of factors: the average molecular weight, polydispersity, degree of substitution of the chains of the initial chlorinated rubber by chlorine (C_3^{Cl}), the nature of the low-molecular aminating agent, and the reaction conditions, i.e., the concentration of the initial products, medium, catalysts, temperature, pressure, and duration of interaction. This dependence, both in the transformations

Fig. 1

Figure 1: Fig. 1

of linear high-molecular compounds into plane-spatial ones and in amination, is statistical in character. Its experimental and theoretical study is associated with great difficulties.

The present work gives the results of an investigation of the heterogeneous amination of solid chlorinated rubber by an aqueous solution of the aminating agent under pressure. First of all, the influence of temperature on the amination process was studied. For this purpose chlorinated rubber of the "Pergut-S" -90 grade was used, containing 63% Cl (i.e., with a degree of substitution of the chains by chlorine according to Korshak (^3) $C_3^{Cl} = 81.5$), and the aminating agent was ammonia in the form of a 26% aqueous solution. The molecular ratio of ammonia to chlorine

in chlorinated rubber was equal to 10 : 1. Six experiments were carried out at intervals of 10° in the range from 95 to 145°.

Under these operating conditions, the following processes were to be expected:

1. Replacement of chlorine atoms by amino groups. It is known that, in low-molecular compounds, this reaction does not stop at the stage of formation of only the primary amine, but proceeds further, at almost the same rate, to the formation of secondary and tertiary amines and a quaternary ammonium base. Under the selected amination conditions, the chlorinated-rubber molecules undergo predominantly micro-Brownian motion. As a result, the introduced primary amino groups will oscillate within a limited range about a mean position, and consequently their collision with chlorine atoms bound to other chains, and their conversion into secondary and tertiary "cross-linking" amino groups, is not the most probable. The formation of quaternary nitrogen bridges must be excluded because of steric hindrance; but even if such bridges are formed at a given moment, they will immediately undergo Hofmann degradation to tertiary nitrogen bridges, with double bonds arising at the corresponding sites of the chains.

Fig. 1

2. Intramolecular and intermolecular dehydrochlorination, of which the former leads to the formation of double bonds, and the latter to the formation of a spatial structure of the product. It should be expected that these processes will proceed rather rapidly, since in a moist medium chlorinated rubber eliminates hydrogen chloride already at 70°(^4). Secondary polymerization cross-linking of the chains through the double bonds being formed is also possible under the amination conditions.

In the reaction products the contents of nitrogen and chlorine were determined,

as well as the ion-exchange capacity in mg-eq/g. In order to facilitate the subsequent discussion, the experimental data were expressed by the corresponding degrees of substitution of chains by chlorine, nitrogen, and nitrogen active in the ion-exchange process: C_3^{Cl}, C_3^{N}, C_3^{Na}. With the aid of these quantities, and knowing $C_{3\,\mathrm{initial}}^{\mathrm{Cl}} = 81.5$ in the original chlorinated rubber, the degree of dehydrochlorination of the chains C_{d} was calculated by the formula $C_{\mathrm{d}} = 81.5 - (C_3^{\mathrm{N}} + C_3^{\mathrm{Cl}})$. The results obtained are presented graphically as functions of temperature. From the graphs in Fig. 1 it is seen that, with increasing temperature, the products become depleted in chlorine owing to the intensive course of the amination and dehydrochlorination processes. The curves C_3^{N} and C_3^{Na} have maxima equal, respectively, to 13.6 at 125° and 2.8 at 115–125°.

These data make it possible to study more deeply the relationship between the ion-exchange capacity of the reaction products and the processes taking place during amination of chlorinated rubber. It is known that the ion-exchange properties of an organic ion-exchanger are associated with the number of electrolyte functional groups contained in it and with steric factors. In our case the electrolyte functional groups are amino groups, and their content is determined through the quantity C_3^{N}. Steric hindrances are due to the degree of formation of a spatial structure, to which the dehydrochlorination processes lead (measured by the quantity C_{d}); and to the content of side groups of the chains—chlorine atoms and methyl groups (measured, respectively, by C_3^{Cl} and C_3^{Me}). The quantity C_3^{Me}

has the same value for all products, since it may be assumed that the polyisoprene skeleton remains unchanged; only C_{d} and C_3^{Cl} are variable. Consequently, their sum $\Phi_{\mathrm{c}} = C_{\mathrm{d}} + C_3^{\mathrm{Cl}}$ is a measure of the factors that create steric hindrance to ion exchange. The steric hindrance to ion exchange, which we denote by P, cannot be identified with Φ_{c}, but at a given temperature it is proportional to Φ_{c}: $P = k\Phi_{\mathrm{c}}$, where k obviously depends on temperature. On the basis of the experimental data it is impossible to construct the actual plots of P and k as functions of temperature, but their form can be determined in the following way. The ratio

$$D = \frac{C_3^{\mathrm{Na}}}{C_3^{\mathrm{N}}}$$

characterizes the accessibility of the amino groups for ion exchange with anions from a solution of a definite concentration (in this case 0.05 n HCl), while the ratio

$$P_{\mathrm{sp}} = \frac{P}{C_3^{\mathrm{N}}}$$

characterizes the spatial hindrances referred to a unit degree of substitution. It is then obvious that

Fig. 2

Figure 2: Fig. 2

$$D = C_3^{\mathrm{Na}}/C_3^{\mathrm{N}} = aC_3^{\mathrm{N}}/k\left(C_{\mathrm{d}} + C_3^{\mathrm{Cl}}\right),$$

where a is a constant independent of temperature. Hence

$$\frac{P}{a} = \frac{C_3^{\mathrm{N}}}{D} = \frac{\left(C_3^{\mathrm{N}}\right)^2}{C_3^{\mathrm{Na}}}; \qquad \frac{k}{a} = \left(C_3^{\mathrm{N}}\right)^2 / C_3^{\mathrm{Na}}\left(C_{\mathrm{d}} + C_3^{\mathrm{Cl}}\right).$$

The plot of the function $\frac{P}{a} = f(t)$ is obtained from the plot of the function $P = f(t)$ by multiplying the ordinates by the constant quantity $1/a$. The functions D, Φ_{c}, and P/a as functions of temperature are shown in Fig. 2.

From the plots in Fig. 2 it is seen that the function $\Phi_{\mathrm{c}}(t)$ has a minimum at 125°, $P/a(t)$ has a minimum at 105° and a maximum at 135°, and $D(t)$ has a maximum at 115° and a minimum at 135°. Since the values of P must be smaller than the corresponding values of $\Phi_{\mathrm{c}}(t)$ (not every elimination of hydrogen halide leads to crosslinking of chains), while $P/a > \Phi_{\mathrm{c}}$, it follows that $a < 1$.

Fig. 2

On the basis of the course of the curves, the following conclusions may be drawn about the influence of temperature on the mechanism of the processes occurring during amination of chlorinated rubber: in the interval 95–105°, the steric hindrances P decrease, and, consequently, dehydrochlorination is predominantly intramolecular; crosslinking of the chains is so slight that it cannot compensate for the decrease in P caused by the intensive decrease of C_3^{Cl} in the product. The increase of P between 105 and 135° shows that intermolecular dehydrochlorination proceeds at an increasing rate. At 135°, the rate of crosslinking of chains by intermolecular dehydrochlorination reaches a value which at higher temperatures remains unchanged or increases so insignificantly that it cannot compensate for the decrease in P caused by the decrease of C_3. As a result, with further increase in temperature P decreases.

In addition to experiments intended to determine the influence of temperature on amination, exploratory experiments were carried out to study the influence of C_3^{Cl} ···

initial chlorinated rubber on amination at a temperature of 125° (the remaining conditions—the ratio between ammonia and chlorinated rubber and the duration of interaction—were kept the same as in the first experiments). The results obtained are given in Table 1.

Table 1

No. of experiment	Cl content in initial chlorinated rubber, %	Cl content in initial chlorinated rubber, C_3^{Cl} init.	Characteristics of the products obtained: Cl, %	Characteristics of the products obtained: Cl, C_3^{Cl}	Characteristics of the products obtained: N, %	Characteristics of the products obtained: N, C_3^N	Characteristics of the products obtained: ion-exchange capacity with respect to 0.05 N HCl, mg-eq/g	Characteristics of the products obtained: ion-exchange capacity with respect to 0.05 N HCl, C_3^{Na}	C_d	D	Φ_c	Π/a
1	38,8	28,8	11,15	6,9	7,0	10,5	2,25	4,7	11,4	44,75	18,3	21,2
2	52,7	54,0	11,20	6,7	7,4	11,0	1,92	4,0	36,3	36,40	43,0	30,6
3	63,0	81,5	9,96	5,9	9,14	13,6	1,36	2,8	62,0	20,80	67,9	197,0

From the data of Table 1 it is evident that, with a decrease in C_3^{Cl} of the initial chlorinated rubber, the values of C_3^N, C_d, Φ_c, and Π/a of the products obtained decrease, while C_3^{Cl}, C_3^{Na}, and D increase. As a result, the product of amination of chlorinated rubber containing 38.8% Cl had an ion-exchange capacity of 2.25 mg-eq/g (with respect to 0.05 N hydrochloric acid). The chlorinated rubbers subjected to amination in experiments Nos. 1 and 2 were obtained by us by the method described below.

Experimental Part

1. Amination of chlorinated rubber with ammonia. 10 g of powdered chlorinated rubber were dispersed, with the aid of 2.56 g of alizarin oil, in 123 ml of 20% aqueous ammonia solution. The suspension was placed in an autoclave of 500 ml capacity and heated for 3 hours at the appropriate temperature in a water or oil bath. The temperature of the latter was regulated with the aid of a contact thermometer. Hydrochloric acid was added to the reaction mixture, and the mixture was filtered. The solid product was washed with water until a negative reaction of the filtrate for chloride ion was obtained, treated with 200 ml of 5% NaOH solution to regenerate its ion-exchange capacity, and filtered again;

it was then washed with distilled water until a neutral reaction was obtained and dried at 90–100°. The nitrogen content of the product was determined by the Kjeldahl semimicro method, and the chlorine content by the method described in (5). The ion-exchange capacity was established by titrating a hydrochloric acid solution of definite concentration after three days' contact with a definite amount of aminochlorinated rubber.

2. Preparation of chlorinated rubber for experiments Nos. 1 and 2 (see Table 1). Chlorine was passed, for a definite time at 45–55°, through a solution of 30 g of natural rubber, plasticized 4 times for 15 min with intervals of 4 hours, and 0.8 g of crystalline iodine in 500 ml of CCl_4. After 1½ hours from the start of the chlorine passage, clarification of the violet-brown solution was observed. After a definite time had elapsed, the solution was poured into boiling water to evaporate the carbon tetrachloride. A white, spongy mass was obtained, which was dried and analyzed for chlorine content. With a two-hour passage of chlorine, chlorinated rubber with a content of 38.8% Cl is obtained, and with a three-hour passage—with a content of 54% Cl.

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Received
3 VII 1956

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Note: Figure translations are in progress. See original paper for figures.