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Superacid Polymers: Paraffin Isomerization and Cracking in the Presence of $AlCl_3$-Sulfonic Acid Resin Complexes

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Polymers were prepared by the reaction of anhydrous $AlCl_3$ vapors with macroporous sulfonic acid resin. HCl was evolved, and a bound complex was formed which incorporated S, Al, and Cl in the ratio 2:1:2. The resin was similar to HSO_4AlCl_2, initially converting *n*-butane into isobutane and *n*-hexane into isomerization and cracking products at temperatures near 100°C. Like HSO_4AlCl_2, the polymer was unstable, rapidly losing Cl during operation. Olefin addition to the paraffin reactants did not significantly affect rates of cracking and isomerization, and this result stands in contrast to those of Pines and Wackher, who used *n*-butane and $AlCl_3$–HCl mixtures. It is suggested that the polymer was capable of protonating paraffins and had a proton-donor strength comparable to that of a superacid solution like SbF_5 + HF.

INTRODUCTION

Strongly acidic polymers have been prepared by the reaction of $AlCl_3$ with sulfonic acid ion-exchange resin; the reaction forms HCl and a polymer-bound complex with a S:Al:Cl ratio of 2:1:2 (*1*). The polymers have been found to have the high reactivity characteristic of very strong proton donors, as shown by conversion data for isomerization and cracking of *n*-hexane at 85°C (*2*). These solids are potentially valuable for study of very strong acids in the absence of the complicating effects of solvents, and their study could provide better understanding of the interactions between Lewis and Brønsted acids and of catalytically active groups formed from them. Since the solids lack the difficulty of separation from reaction products and the corrosiveness that characterize solutions, they could perhaps be of practical interest as hydrocarbon conversion catalysts; their lack of stability, however, weighs against this prospect (*2*).

The research described here was intended to be a beginning investigation of the reactivity and stability of the polymers. The reactions chosen for study were among the simplest of the paraffin conversions which may take place via proton donation reactions. Most of the experiments were done with polymers contacting *n*-butane, which was converted into isobutane, and a few experiments were done with *n*-hexane, which gave a distribution of isomerization and cracking products.

NOMENCLATURE

P_b	Partial pressure of *n*-butane, atm
r	Rate of *n*-butane isomerization, moles/sec g
R	Gas constant, 1.987 cal/mole°K
T	Temperature, °K

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EXPERIMENTAL METHODS

Polymers were prepared by contacting macroporous sulfonated poly(styrene-divinylbenzene) beads (some containing $-SO_3Na$ as well as $-SO_3H$ groups) with anhydrous $AlCl_3$ vapors at 115°C, as described in detail elsewhere (*1*). The polymers were tested in a flow reactor fed with hydrocarbon vapors usually diluted with He. The flow system was stainless steel, and the tubular reactor (40 cm long and 2.5 cm o.d.) was mounted vertically in an 800-W Lindberg electric furnace. The power input to the furnace was regulated by a proportional controller (RFL Industries, Model 70), and the reactor temperature was controlled stably at temperatures from 70 (±0.2) to 141 (±0.4)°C. The reactor exit stream was connected to the gas sampling valve of a gas chromatograph (Hewlett-Packard, Model 5750) interfaced to a quadrupole mass spectrometer (Hewlett-Packard, Model 5930A).

Prior to an experiment, the flow system was baked out and purged with dry He; dry beads of resin and glass were mixed and weighed into the reactor, which was then heated for about 2 hr until the desired temperature was reached. The flows of He and hydrocarbon were then begun at the desired rates. The hydrocarbon reactant was either *n*-butane from a cylinder (Union Carbide CP Purity Grade containing 1710 ± 50 ppm of isobutane, the only impurity detected by gas chromatography), or *n*-hexane (Phillips Research Grade with a specified purity of 99.99 mole%) fed from a syringe pump.

During an experiment, the flow rates and temperatures were held constant for 2–11 hr, and the product stream was periodically sampled and analyzed. The conversions were determined from gas chromatographic analysis of products on a *n*-octane on Porasil C (150–200 mesh) column (Waters Associates) held at 28 and 60°C for butane and hexane feeds, respectively. Each product was identified by its mass spectrum. Occasional experiments were also performed with *n*-butane feeds mixed with butene-1 and *n*-hexane feeds mixed with H_2.

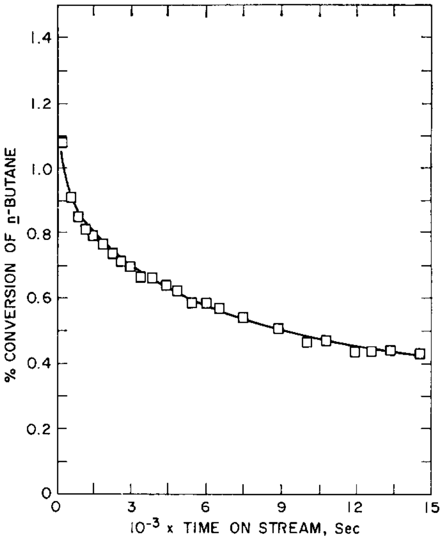

FIG. 1. Isomerization of *n*-butane in a flow reactor at 109°C. The polymeric reactant was prepared from $AlCl_3$ and sulfonic acid resin (Sample 2, Table 1). The partial pressure of *n*-butane was 0.77 atm, and the space velocity was 2.72×10^{-6} moles of *n*-butane/(g of polymer sec).

Fresh and used polymers were analyzed for Al, Cl, S, and Na; the methods are given in a separate report with more detailed analyses of the polymers (*1*). All the experimental details have been described by Magnotta (*3*).

RESULTS

Representative data (Fig. 1) show that the conversion of *n*-butane into isobutane (the only observed product in the effluent stream) decreased rapidly as the experiment progressed. The rate of loss of reactivity decreased with increasing time on stream [and no simple mathematical expression gave a good representation of the data (*3*)]. The results of the experiment represented by the data of Fig. 1 show that only 0.2 mmoles of isobutane had been pro-

TABLE 1

Analysis of Fresh and Used Polymers

	Fresh polymers							Used polymers								
Sample No.	Composition (wt%)				Atomic ratios			Run temp (°C)	Turnovers (No. of molecules converted/Al atom)	Composition (wt%)				Atomic ratios		
	S	Cl	Al	Na	Cl:Al	Al:S	Na:S			S	Cl	Al	Na	Cl:Al	Al:S	Na:S
1[a]	12.6	13.6	4.44	0.00	2.34	0.42	0.00	85.0	0.34	10.8	11.2	4.39	0.00	1.94	0.48	0.00
2[b]	11.8	14.2	4.95	0.00	2.19	0.50	0.00	106	0.14	12.0	13.6	4.80	0.00	2.15	0.47	0.00
								106	0.49	10.3	11.6	4.97	0.00	1.78	0.57	0.00
								141	0.12[c]	13.8	11.5	6.01	0.00	1.46	0.52	0.00
3[b]	9.30	29.2	7.02	2.83	3.17	0.90	0.42	108.5	0.22	2.80	25.4	7.01	3.49	2.76	2.97	1.74
								107.6	0.26	4.41	25.8	6.82	3.22	2.88	1.84	1.02
4[b]	7.21	38.3	8.99	3.53	3.26	1.47	0.68	107	0.10	5.28	34.1	8.93	3.61	2.91	2.01	0.95

[a] Used for *n*-hexane conversion.

[b] Used for *n*-butane conversion.

[c] Polymer lost reactivity very rapidly, and precision is low.

duced per gram of polymer when the experiment was terminated; since the polymer contained about 2 mmoles of Al-containing groups/g, the result corresponds to a total turnover of only about 1 reactant molecule/10 of the groups which might be expected to form the proton donor sites (*1*).

Because the loss of polymer reactivity was rapid, emphasis was placed on obtaining precise reaction rate data for short onstream times so they could be extrapolated to zero time of contact between the hydrocarbon reactants and polymers. Correspondingly, *n*-butane conversion experiments were done with a series of fresh polymer charges, all from the same synthesis batch, for which the analytical results are given in Table 1 (sample 2) (*1*). Conversion–time data like those of Fig. 1 were obtained for feeds of various *n*-butane partial pressures in He and for various temperatures. The data were extrapolated to zero contact time,[2] providing initial conversion for characterization of the fresh polymer.

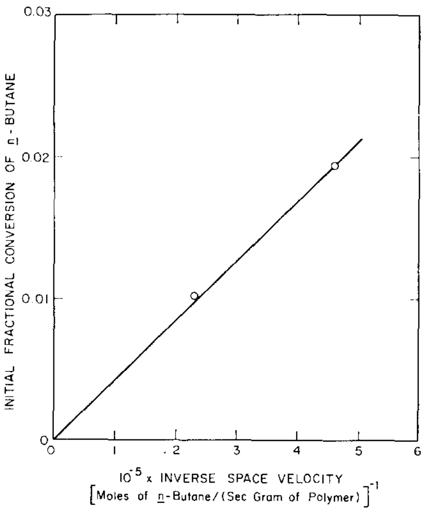

FIG. 2. Differential conversions of *n*-butane at 106°C in the presence of fresh polymer (Sample 2, Table 1).

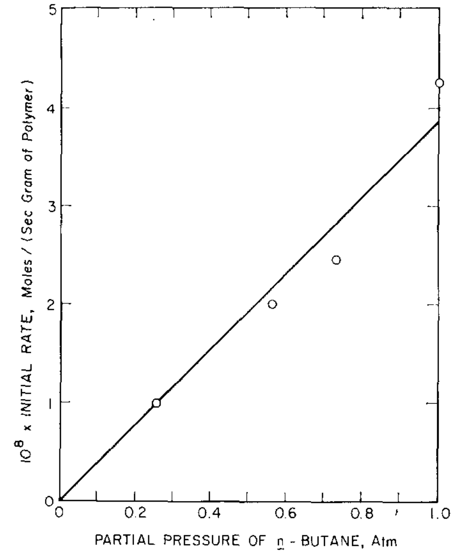

FIG. 3. First-order dependence of *n*-butane isomerization rate. Data were extrapolated to zero paraffin–polymer contact time and were adjusted to 106°C with Eq. (1).

Differential conversions were observed, as demonstrated by the linearity of a plot of initial conversion against inverse space velocity (Fig. 2), and therefore reaction rates could be calculated directly from the data. The rate was proportional to the *n*-butane partial pressure (Fig. 3), and the activation energy determined from an Arrhenius plot (*3*) was 8.3 ± 0.9 kcal/mole. The rate data for the fresh polymer are therefore summarized as

$$r = 0.0025e^{-8300/RT}P_b, \qquad (1)$$

where the rate, r, has dimensions of moles/(sec g of polymer).

Experiments like those just described were carried out with sulfonic acid resin to which no $AlCl_3$ had been added and with unsulfonated, macroporous poly(styrene-divinylbenzene) containing deposits of $AlCl_3$ (*1*). Neither the polymer with Brønsted acid groups alone nor the polymer with Lewis acid groups alone caused detectable conversion of paraffin. The only resins found to be reactive were those which con-

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[2] Plots of log (conversion) vs time were used for the extrapolation; zero paraffin–polymer contact time was slightly different from zero on-stream time, corresponding to the delay time in the feed lines (*3*). The small effects of loss of polymer reactivity during the initial heating prior to reaction were neglected.

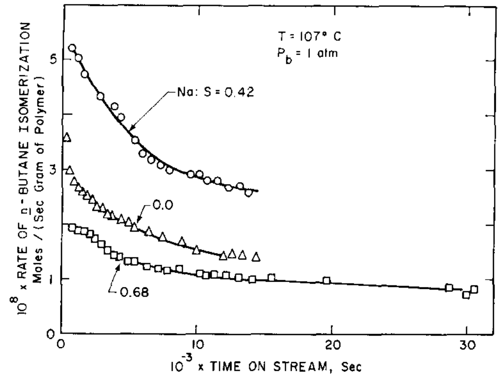

FIG. 4. Rates of isomerization of *n*-butane in the presence of polymers prepared from $AlCl_3$ and resins of various concentrations of $-SO_3H$ and $-SO_3Na$ groups (Table 1). Rates are based on the initial mass of polymer, which changed in operation. Rates were adjusted slightly to 107°C and 1 atm based on Eq. (1).

tained complexes formed from $AlCl_3$ and $-SO_3H$ groups.

Polymers were also prepared from $AlCl_3$ and resins containing $-SO_3Na$ groups, which had been formed by ion exchange of a fraction of the $-SO_3H$ groups [Table 1 (*1*)]. Rate data are shown in Fig. 4 for three different polymers in which 0, 42, and 68%, respectively, of the $-SO_3H$ groups had been replaced by $-SO_3Na$ groups before addition of $AlCl_3$. The behavior of all three samples was similar; the polymer in which 42% of the $-SO_3H$ groups had been replaced by their salts appeared to be more reactive than polymers containing either more or less Na, but in view of the reproducibility of data from run to run, it is doubtful that the difference is significant.

The polymer with 42% of the $-SO_3H$ groups replaced by $-SO_3Na$ groups was also used in an experiment with *n*-butane feed containing 0.92 ± 0.02% butene-1 to test for a possible effect of the olefin on the reactivity. The added butene was found to have a small effect on the rate–time curve (Fig. 5).

Conversions of *n*-hexane in the presence of a polymer prepared from sulfonic acid resin and $AlCl_3$ have been reported previously (*2*). In further experiments, initial conversions of 40–80% have been observed at 85°C and inverse space velocities between about 1×10^6 and 2×10^6 (g of polymer sec)/mole of *n*-hexane. The products were saturated C_3–C_5 hydrocarbons and branched C_6 isomers, and the yield of the cracking products decreased more rapidly with on-stream time than did the yield of isomerization products. Since no olefinic cracking products were observed, these results are consistent with the suggestion that hydrogen was provided to the cracking products by the acidic polymer.

Reaction of *n*-hexane in the presence of H_2 instead of He was also studied. The conversion data for *n*-hexane at a partial pressure of 0.33 atm indicated that H_2 at a partial pressure of 0.67 atm had no discernible effect on the polymer reactivity. Further, addition of 0.1 mole% hexene-1 evidently had no effect on the *n*-hexane conversion data.[3]

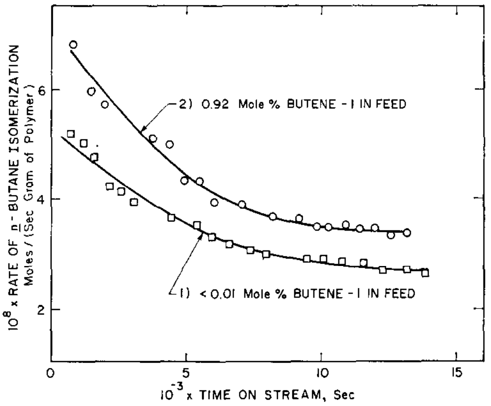

FIG. 5. Effect of butene-1 addition on the rate of *n*-butane isomerization. 1) Reaction without added butene-1 at 1 atm and 108.5°C and a space velocity of 1.7×10^{-6} moles of *n*-butane/(g of polymer sec); 2) reaction with 0.92 ± 0.02 mole% butene-1 in feed at 1 atm and 107.6°C and a space velocity of 1.7×10^{-6} moles of *n*-butane/(g of polymer sec). The polymer was sample 3 (Table 1).

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[3] The *n*-hexane conversion experiments with and without olefin were, however, done at space velocities differing by a factor of 2 and were therefore not entirely comparable, so some small effect of olefin cannot be ruled out.

Analyses of fresh and used polymer samples from a number of the experiments described above are summarized in Table 1. The data indicate significant losses of components during operation. The Cl:Al ratio of the Na-free samples (1 and 2) decreased from initial values of about 2[4] to as little as 1.5. During operation, the samples lost Cl (and possibly H) as well as small amounts of S. The Cl loss increased with increased reaction temperature and with increased time of operation. It might be speculated that one Cl atom was lost for each molecule of hydrocarbon converted, but the precision of the data is not good enough to test this possibility (Table 1). In contrast to the Na-free polymers, those prepared from resins containing $-SO_3Na$ as well as $-SO_3H$ groups lost no significant amounts of Cl during operation, but they all lost S. No tar or coke was found in any of the used samples.

DISCUSSION

The rates of reaction of *n*-butane and of *n*-hexane in the polymer were independent of the influence of mass transfer in the external gas phase and in the macropores, as determined by standard criteria (*3*). The Al and Cl components were incorporated throughout the microspheres constituting the polymer mass, as shown by the stoichiometry of the synthesis (Table 1). Since the microspheres were highly cross-linked, nonporous, and unswollen, it is likely that the paraffin reactant molecules encountered significant diffusion resistance and were unable to penetrate uniformly into the microspheres containing the Al and Cl. The data do not allow a quantitative evaluation of the mass transfer influence, but the likelihood of its importance implies that the parameters of Eq. (1) do not represent intrinsic kinetics. Since the measured rate of *n*-butane isomerization in the presence of the fresh polymer at 107°C was of the order of 10^{-5} moles/(Al ion sec), this value provides a lower limit of the reaction rate per protonic site.

The results are generally consistent with a large body of information indicating the role of strong proton donors in the polymer and of carbonium ion intermediates in the paraffin transformations (*4*). The results reported by Pines and Wackher (*5*) showed that isomerization of *n*-butane in the presence of $AlCl_3$ and HCl can be initiated by protonation of small amounts of olefins to give carbonium ions, which are converted in a cycle of hydride abstraction and carbonium ion rearrangement reactions. The paraffin conversions in the presence of the polymer might similarly be expected to be initiated by protonation of olefin impurities in the feeds. The data for olefin-spiked feeds, however, appear to be at odds with this expectation. An increase in the butene-1 concentration in the *n*-butane feed from <0.01 to 0.92 mole% appeared to cause roughly a 30% increase in the rate of *n*-butane isomerization in the presence of the polymer (Fig. 5); this apparent increase corresponds approximately to the scatter in the rate data, and the only conclusion, therefore, is that the presence of the added butene-1 had little effect on the isomerization rate. This result stands in contrast to the results of Pines and Wackher (*5*), who found, for example, that an increase in concentration of butenes from 0.015 to 0.3 mole% in *n*-butane led to an increase in *n*-butane conversion from 12 to 27% with $AlCl_3 + HCl$ at 100°C; similarly, an increase in concentration of butenes from 0.03 to 0.6 mole% in *n*-butane led to an increase in *n*-butane conversion from 2 to 66% with $AlBr_3 + HBr$ at 25°C.

We speculate on the basis of the above comparison that the new polymers may be comparable in their proton-donor strengths

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[4] The Cl:Al ratios were initially slightly in excess of 2 because $AlCl_3$ deposits were present in addition to the complex having a Cl:Al ratio of 2 (*1*).

TABLE 2

Some Catalyst Systems for Hydrocarbon Reactions Prepared from Lewis and Brønsted Acids

Ref.	Lewis acid	Brønsted acid	Catalyst[a] composition	Reactions and conditions
Schmerling and Ipatieff (*9*)	$AlCl_3$	H_2SO_4	HSO_4AlCl_2	Isobutane–propylene alkylation at 40°C and *n*-heptane isomerization at 125°C in the presence of HCl promoter.
Kluge and Moore (*10*)	$AlCl_3$	RSO_3H	RSO_3AlCl_2	Phenol–(propylene oligomer) alkylation at 80°C.
Topchiev *et al.* (*11*)	$AlCl_3$	H_2SO_4	HSO_4AlCl_2	Benzene–isopropylchloride alkylation and related reactions.
Kelly (*12*)	BF_3	Gel form sulfonic acid resin	Undetermined	Isobutane–ethylene alkylation at temperatures near 25°C.
Huang and Yurchak (*13*)	BF_3	Macroporous sulfonic acid resin	Undetermined	Isoparaffin–olefin alkylation at −20 to 20°C in a flow system with recycled BF_3.

[a] Proton donor species were presumably also present.

to the superacid solutions like $SbF_5 + HF$ and $SbF_5 + FSO_3H$, which may protonate paraffins and initiate isomerization, cracking and alkylation reactions at 25°C (*6–8*). This speculation forms the basis for the following working hypothesis of the structures formed in the polymer.

Neither $-SO_3H$ groups alone nor $AlCl_3$ alone in the polymer caused observable *n*-butane conversion, but a combination of the two was highly reactive toward *n*-butane. It follows that species formed from $-SO_3H$ groups and $AlCl_3$ constituted the reaction sites. The analyses of polymer samples indicate that a complex was formed, incorporating Al and Cl in the ratio 1:2; this complex is inferred to be similar to the complex HSO_4AlCl_2, which is formed from $AlCl_3$ and H_2SO_4 (*9*). The latter complex, when promoted by HCl, is reported to form a correspondingly active catalyst system for paraffin conversion (*9*), and we suggest that it is but one of a class of related catalyst systems that have been prepared, for example, from $AlCl_3$ and monomeric Brønsted acids and from BF_3 and sulfonic acid resins (Table 2). The structures of the proton donor species formed from these complexes have not been determined.

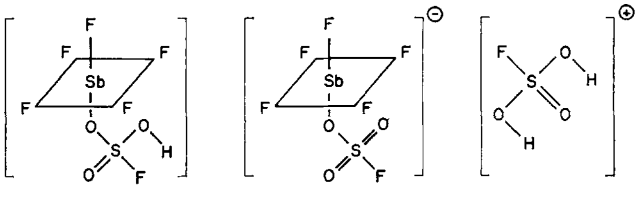

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Fig. 6. Some structures existing in solutions of $SbF_5 + FSO_3H$ (*14–16*).

Structures existing in the superacid solution $SbF_5 + FSO_3H$ have, however, been determined by nmr and Raman spectroscopy (Fig. 6) (*14–16*). Pursuing the presumed similarity between the superacid solution and the polymer, we suggest by analogy that the structures shown in Fig. 7 may exist within the polymer. Structure VI, a very strong proton donor, is suggested to exist in equilibrium with structures IV and V and to be responsible for the observed hydrocarbon conversions, being capable of protonating straight-chain paraffins. Structure IV would be expected to be unstable toward loss of HCl, just as is HSO_4AlCl_2, which forms SO_4AlCl (*9*). The splitting off of HCl would account for the observed loss of Cl from the polymer[5] and the accompanying loss of reactivity, presumably as a result of the loss of Brønsted acidity residing in structures IV and especially VI. Analogously, HSO_4AlCl_2 has been found to lose most of its apparent catalytic activity upon loss of HCl; the hindrance of such a deactivation explains the use of HCl as a promotor (*9*). The polymer might analogously be expected to be stabilized by the addition of HCl to the reactants, and therefore with HCl it might be expected to form an analogous catalytic system for hydrocarbon isomerization, alkylation, and cracking.

Note added in proof: A recent patent (*17*) reports solids prepared from SbF_5 and sulfonated (or fluorinated) Al_2O_3. These inorganic solids are evidently quite similar to the organic solids reported here. For example, (1) isomerization of *n*-butane took place at roughly the same rate in the presence of the solid derived from sulfonated Al_2O_3 as in the presence of the polymer; (2) although the inorganic solids were referred to as catalysts for many paraffin conversions, no stability data were given, and we suggest that the inorganic solids, like the polymers, may instead be reagents; in agreement with the suggestion of the preceding paragraph, it was stated (*17*) that HF may be added to the hydrocarbon feedstock to compensate for any HF removed from the catalyst during the course of the reaction.

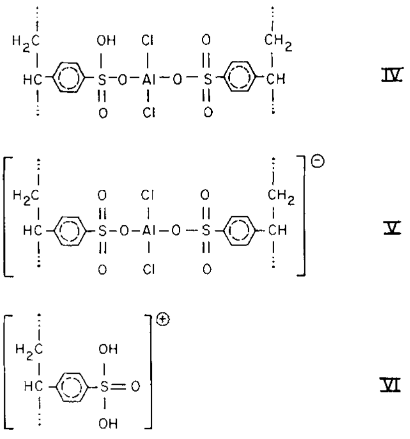

Fig. 7. Structures postulated to exist in the strongly acidic polymer.

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[5] The loss of S from the samples containing Na is not explained, but a speculative suggestion is that a complex such as IV, perhaps after splitting off HCl, forms salt-like structures with $-SO_3Na$ groups, which are unstable to the loss of SO_2.

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