April, 1974] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(4), 829—831 (1974) 829

Novel Radical Salt Polymers as Hydrogenation Catalyst of α-Olefins

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(Received October 4, 1973)

Novel polymeric radical salts prepared by inserting alkali-metals into semi-conductive polymers derived from poly(tetrahalophenylene sulfides) were found to be effective hydrogenation catalyst for α-olefins; their activity trends as to the sort of alkali-metal and halogen of the matrix polymer were Cs>K>Na and F>Cl>Br respectively. The catalyst also showed an activity for the *cis-trans* isomerization of hex-2-ene which was proportional to that for the hydrogenation. The activities of the catalyst were discussed in terms of its steric confinement.

The enhanced *para-ortho* hydrogen conversion catalysis[1] found for polymeric radical salts prepared by alkali-metal insertion into poly(tetrahalophenylene sulfides) and the semi-conductive polymers derived therefrom[2] prompted us to examine their catalytic activity for the hydrogenation of unsaturated compounds. Along these lines, we investigated the hydrogenation activity of these novel polymeric radical salts for some olefins referring to their *para-ortho* hydrogen conversion activity. We will report here that the present radical salts, despite a lack of metal with a d-electron shell, are effective hydrogenation catalysts for α-olefins.

Experimental

Hydrogenation was carried out at 140 °C for 3 hr in an autoclave (volume, 100 ml) containing 4 ml of olefin, 0.5 g of the radical salt, and hydrogen pressurized up to 35 kg/cm^2 unless otherwise noted. The reaction products were identified with authentic samples and were quantitatively determined by using gas-liquid partition chromatography (DMS 30 wt%, 6 m).

Commercial reagents, hex-1-ene, hex-2-ene, 4-methylpent-1-ene, 4-methylpent-2-ene, and cyclohexene were purified by distillation over metallic sodium. Propylene, but-1-ene, and *cis*-but-2-ene in commercial cylinders were simply dried over calcium hydride. All the olefins were confirmed before use to contain no appreciable amount of any impurity detected by the glc.

The radical-salt complexes were prepared by bringing poly(tetrahalophenyl sulfides) or semi-conductive polymers (*vide infra*) into contact with alkali-metal vapor in a vacuum at the evaporation temperature of alkali-metals up to their saturated insertion into the polymers. The amounts of the inserted alkalimetals were determined by means of atomic-absorption spectroscopy.

We utilized poly(tetrahalophenylene sulfides) prepared by careful polycondensation of sodium pentahalothiophenoxide, and semi-conductive polymers prepared by a dehalogenation condensation of poly(tetrahalophenylene sulfides), as described previously.[2] In this investigation we also used new semi-conductive polymers which were obtained by treating the radical salt complexes with water in a Soxhlet extractor for an extended period until no trace of alkali-metal was detected in the extract. Some characteristics of those modified semi-conductive polymers are given in Table 1, together with those of the poly(tetrahalophenylene sulfides) and semi-conductive polymers previously prepared.

TABLE 1. CHARACTERISTICS OF ACCEPTOR POLYMERS

Acceptor polymers[a]	Elemental Analysis, %					Free spins per g
	C	H	N	X	S	
PTF	40.2	0	0	—	19.0	nil
PTCl	29.3	0	0	57.4	12.8	nil
PTBr	18.9	0	0	73.0	8.0	nil
SMF	44.8	0.7	2.9	—	18.0	1.2×10^{16}
SMCl	40.8	1.2	3.1	38.9	12.5	4.2×10^{18}
SMBr	26.6	0.5	1.8	61.0	8.5	1.2×10^{18}
mSMF	60.3	1.8	5.4	—	11.2	1.8×10^{19}
mSMCl	76.0	2.9	9.0	1.9	2.7	8.1×10^{18}
mSMBr	62.5	2.8	7.7	2.9	10.5	4.0×10^{18}

a) PTX (X : F, Cl, Br), SMX (X : F, Cl, Br) and mSMX (X : F, Cl, Br) are abbreviations for the poly(tetrahalophenylene sulfides), the semi-conductive polymers, and the modified semi-conductive polymers, respectively, mentioned in the text. mSMX(X : F, Cl, Br) were prepared from SMX–Cs(X : F, Cl, Br) radical salts (see Table 3)

The free spin concentrations of the acceptor polymers and the radical-salt complexes were determined by means of their ESR spectra measured at 9000 MHz in 100 kHz modulation, in comparison with the DPPH spectra obtained under the same operating conditions as with the polymers and the complexes.

Results and Discussion

Table 2 shows the results of the hydrogenation of some olefins in the presence of the semi-conductive polymer alkali-metal complexes as catalyst. It can be seen that the present catalyst hydrogenates α-olefins fairly well, but not inner olefins and cyclic olefins. This may be interpreted as a consequence of the severe steric requirements of the present catalyst, which controls an effective interaction with olefins on the surface of the catalyst.

Thus, the study was focused on the ·hydrogenation activity of the polymeric radical salt for α-olefin, *i.e.*, hex-1-ene. The results of the hydrogenation of hex-1-ene in the presence of the poly(tetrahalophenylene sulfide)–Cs complex and the semi-conductive polymer–Cs complex are given in Table 3. The hydrogenation

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Table 2. Hydrogenation of olefins with the radical salt polymers

Olefins	Radical salts	Conversion, %	Selectivity, %
Propylene[a]	SMBr-K	90	100
But-1-ene[a]	SMBr-K	99	60
cis-But-2-ene[a]	SMF-K	—	0
Hex-1-ene	SMCl-Cs	50	24
Hex-2-ene	SMCl-Cs	—	0
4-Methylpent-1-ene	SMCl-Cs	31	40
4-Methylpent-2-ene	SMCl-Cs	—	0
Cyclohexene	SMCl-Cs	0	0

a) Olefin 200 mmHg and H_2 300 mmHg were introduced into a 300 ml volume reactor containing SMX (X : F, Br) 0.2 g and distilled potassium 0.3 g, the hydrogenation being carried out at 100°C for 2.5 hr.

selectivity was low because of the concurrent isomerization of hex-1-ene to hex-2-ene; however, the activity of the present catalyst can be fully appreciated when one considers that no hydrogenation of hex-1-ene occurred in the presence of alkali-metal alone under the same reaction conditions. Further, the present catalysts incorporating the halogen were more effective on the hex-1-ene conversion, and hence on the hexane yield, than the poly(phenylene sulfide)–Cs complex (abbreviated as PPS–Cs), which contained no halogen, although the *para-ortho* hydrogen conversion activity of the PPS–Cs, as is shown in Table 3, was not inferior to that of the present catalysts. Here, it should be noted that the *cis*/*trans* isomer ratios of the hex-2-ene isomerized from hex-1-ene were larger than the thermodynamic equilibrium ratio about 0.43.† This suggests a correlation between the hydrogenation and the *cis-trans* isomerization activity of the catalyst, as will be discussed below in conjunction with a later experiment.

In spite of the characteristics detailed above, the rather poor activity of the hydrogenation, together with the obscure activity trend as to the sort of halogen, forced us to prepare the catalyst more elaborately. The poor activity was considered to be due to a partial destruction of the radical-salt structure of the catalyst, followed by the formation of alkali-metal halide. The catalysts were, therefore, treated with water (see Experimental) to remove the alkali-metal halide, thus giving newly modified semi-conductive polymers from which we could again prepare radical salts of alkali-metals.

The results of the hydrogenation of hex-1-ene in the presence of these modified radical salt polymers are given in Table 4. It can be seen that there is a clear trend for the activities of the catalysts as to sort of halogen and also as to sort of alkali-metal, together with enhanced hydrogenation activity as was collated by their extraordinarily high *para-ortho* hydrogen conversion rate constant.

This activity trend, increasing towards the catalyst with less electronegative alkali-metals, has frequently been observed in radical salts previously studied.[4,5] It should be interpreted on the basis of the nature of alkali-metals, *viz.*, the ionization potential, the electron affinity, the ion radius, and finally the structure of the catalysts in which alkali-metals are located.

The activity trend for this sort of halogen—*viz.*, the larger the electronegativity of halogen, the stronger the hydrogenation activity—is the first experimental evidence, as far as we are aware, as to radical salts containing halogen; however, the extremely low halogen content of the catalyst (see Table 1) compels us to postpone a discussion of the role of the halogen until a structural elucidation of the catalyst has been made.

Table 3. Hydrogenation of hex-1-ene with the radical salt polymer

Radical salts	Cs inserted wt%	Conversion, %	Selectivity, %	Hex-2-ene isomer ratio, *cis*/*trans*	*Para-ortho* conversion rate const. at 20 °C min^{-1}
PTF-Cs	57.2	73.2	14.4	0.56	1.9×10^{-1}
PTCl-Cs	68.8	79.6	27.3	0.82	3.7×10^{-1}
PTBr-Cs	70.2	40.5	23.3	0.47	1.2×10^{-1}
SMF-Cs	70.0	32.6	16.6	0.62	1.2×10^{0}
SMCl-Cs	77.6	49.7	23.9	0.52	2.3×10^{-1}
SMBr-Cs	79.5	53.0	61.3	1.4	2.0×10^{-1}
PPS-Cs	—	17.2	20.3	—	3.0×10^{-1}

Table 4. Hydrogenation of hex-1-ene with the modified radical salt polymer

Radical salts	Alkali-metal wt%	Conversion, %	Selectivity, %	Hex-2-ene isomer ratio, *cis*/*trans*	*Para-ortho* conversion rate const. at 20 °C, min^{-1}
mSMF-Cs	62.2	100	90.5	3.8	2.5×10^{0}
mSMF-K	60.7	90.0	80.3	3.1	—
mSMF-Na	62.3	78.6	67.0	1.8	—
mSMCl-Cs	76.9	99.6	83.7	2.8	1.8×10^{0}
mSMBr-Cs	71.4	85.4	24.0	1.7	2.5×10^{-1}

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† This value was obtained in the glc analysis of commercial hex-2-ene.

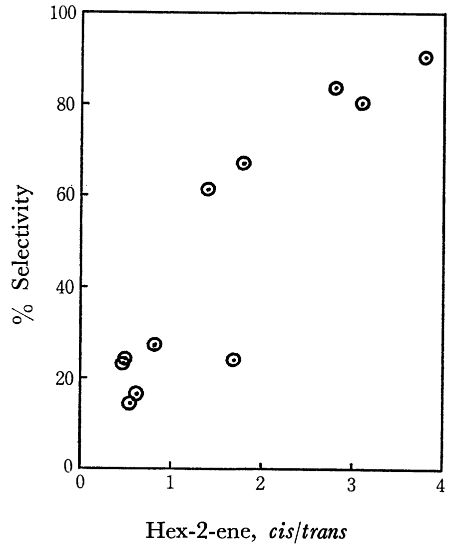

Fig. 1. A correlation between the selectivity in the hydrogenation of hex-1-ene and the *cis*/*trans* isomer ratio of hex-2-ene.

Also notable was a prominent elevation of the *cis*/*trans* isomer ratio of the hex-2-ene isomerized from hex-1-ene, as may also be seen from Table 4. The relation between the hydrogenation selectivity of hex-1-ene and the *cis*/*trans* isomer ratio of hex-2-ene, by using the values in Tables 3 and 4 is shown in Fig. 1. In the present catalyst the hydrogenation activity for hex-1-ene is nearly proportional to the *cis-trans* isomerization activity for hex-2-ene. This result confirms the correlation between the hydrogenation and the *cis-trans* isomerization activity of the catalyst. The linear relation and the high *cis-trans* isomer ratio at high selectivity imply that the active site for the hydrogenation is also active for the *cis-trans* isomerization. The steric requirement of olefins for the hydrogenation and the activity for the *cis-trans* isomerization process lead us to suspect that the active site of the catalyst consists of a sterically-confined structure.

Thus, attention should again be directed to the structural characteristics of the catalysts, especially those of the acceptor polymers prepared through the extraction; however, because of the scarcity of appropriate analytical methods, only their element compositions and free spin concentrations have been collected (Table 1). As was noted in a previous paper,[2] the semi-conductive polymers tightly bind the pyridine used in the preparation. Although the bound pyridine remained, giving rise to its enriched presence in the extracted polymers (Table 1), it could not execute a dramatic enhancement in the hydrogenation activity since no activity difference was observed between the radical salts from poly(tetrahalophenylene sulfides) and those from the semiconductive polymers. One rather troublesome thing for the enhancement might be the role of oxygen, which mainly filled[††] the residual composition, amounting to about 10%, of the extracted polymers, besides the role of the halogens, as has already been noted. In addition, it may be useful to note that the extracted polymers have no hydrogen bound by any such reaction as an ion exchange of alkali-metals in the radical salt polymer with the water, since the binding of alkali-metals in the radical salt was considered to be a loose one which lead to such reaction as hydrogen evolution.

In any case, however, the increase in the free-spin concentrations of the extracted polymers from that of the original polymer might lead to some inferences, such as that the extracted polymers came to have largely developed conjugated networks favorable for the accommodation of large amounts of free spins, thus increasing the sterically-confined active sites for the hydrogenation.

Eventually, the low content of halogen and the large amount of free spins in the extracted polymer may be a consequence of the acceptor polymer acquiring a structure functionable for the present catalysis at high densities.

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[††] Among the extracted polymers, mSMCl and mSMBr gave 6.3% and 9.6% oxygen respectively (see Table 1).