Novel Radical Salts Polymer Catalyst Carrying Enhanced Para-Ortho-Hydrogen Conversion

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The catalytic behaviour of aromatics-alkali metal ion radical salts has been extensively studied since the disclosure of the catalytic activity of the tetracyanopyrene-cesium complex in the hydrogen-deuterium exchange reaction.[1] In this paper, we will establish that novel polymeric radical salts obtained by alkali metal insertion into poly(tetrahalophenylene sulphide)s and into semiconducting materials derived therefrom exhibit a strongly enhanced catalytic activity in para-ortho-hydrogen conversion.

The poly(tetrahalophenylene sulphide)s were prepared by the careful polycondensation of sodium pentahalothiophenoxide, while the semiconducting materials were obtained by dehalogenating poly(tetrahalophenylene sulphide)s in the presence of polar solvent such as pyridine at about 200°C. A possible structure of these semiconducting materials as likely to consist of a dibenzothiophene nucleus was suggested in a preceding paper,[2] along with the details of their preparations.

The radical salts complexes were easily obtained by placing the poly(tetrahalophenylene sulphide)s or the semiconducting materials in contact with alkali metal vapour in vacuum at the evaporation temperature of the alkali metal.

Table 1 shows the characteristics of the resulting complexes, which were obtained by inserting the Cs metal into the acceptor polymers to approximately saturation amounts. In spite of much occlusion of the Cs metal, the resulting complexes were stable in air—*i.e.*, they were not inflammable and did not show a rapid decomposition, though they absorbed much gaseous oxygen and humidity,—contrary to the generally-accepted idea of the unstable character of the organic-alkali metal ion salts. It is apparent that the stability of the complexes does not depend on the fact that the acceptor is simply polymeric, since we have confirmed that the complexes[3] of alkali metal poly(phenylene oxide) and alkali metal poly(phenylene sulphide), which constitute the basic skeleton of the poly(tetrahalophenylene sulphide)s, cause a rapid decomposition when in contact with air. The stability may be due to some specific structure of the semiconducting materials formed by the dehalogenation of the poly(tetrahalophenylene sulphide)s.

The para-ortho-hydrogen conversion on these complexes as catalysts was conducted in a manner analogous with that preported previously.[4] The same table, Table 1, summarizes the rate constants of the hydrogen conversion obtained by assuming a first-order reaction and the activation energies of the conversion. As is seen from Table 1, the rate constants in the range of 10^{-1}—10^{0} min^{-1} are obviously extraordinarily high, since the rate constants of the radical-salt catalysts so far studied have lain in the range of 10^{-2}—10^{-4} min^{-1}.[5]

At any rate, the high rate constants indicate enhanced catalytic activities of the present complexes in hydrogen-participating reactions. Applications of the present new catalysts to these reactions are in progress, along with the more precise elucidation of the relation between the para-ortho-hydrogen conversion and their structures.

Table 1. The electrical resistivity, the spin concentration, the rate constant (k), and its activation energy (E) of the para-ortho-hydrogen conversion of poly(tetrahalophenylene sulphide)-Cs and the semiconductive polymer-Cs complex

Complex[a]	Elemental analysis of acceptor polymer (%)			Cs inserted (wt%)	Resistivity at 20°C (Ω·cm)	Concentration of free spin per g	k at 20°C (min^{-1})	E (kcal/mol)
	C	Halogen	S					
PTF-Cs	40.2	—	19.0	57.2	2.0×10^{2}	2.7×10^{17}	1.9×10^{-1}	—
PTCl-Cs	29.3	57.4	12.8	68.8	1.8×10^{4}	1.8×10^{18}	3.7×10^{-1}	—
PTBr-Cs	18.9	73.0	8.0	70.2	—	4.0×10^{19}	1.2×10^{-1}	—
SMF-Cs	44.8	—	18.0	70.0	—	1.1×10^{18}	1.2×10^{0}	—
SMCl-Cs	40.8	38.9	12.5	77.6	4.0×10^{2}	9.6×10^{19}	2.3×10^{-1}	4.0
SMBr-Cs	26.6	61.0	8.5	79.5	3.0×10^{-1}	1.1×10^{19}	2.0×10^{-1}	5.7

a) PTF, PTCl, and PTBr are abbreviations for the poly(tetrahalophenylene sulphide) in which the halogens are fluorine, chlorine, and bromine respectively. SMF, SMCl, and SMBr are abbreviations for the semiconductive polymers, mentioned in this paper, derived from PTF, PTCl, and PTBr respectively.

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[1] T. Kondow, H. Inokuchi, and N. Wakayama, *J. Chem. Phys.*, **43**, 3776 (1965).

[2] H. Kawazura and T. Taketomi, *Polym. Lett.*, **B10**, 265 (1972).

[3] These were obtained by a procedure analogous with that of the preparation of the complexes of poly(tetrahalophenylene sulphide)s.

[4] H. Inokuchi, N. Wakayama, T. Kondow, and Y. Mori, *J. Chem. Phys.*, **46**, 837 (1967).

[5] See, for example, Y. Mori, N. Wakayama, and H. Inokuchi, *J. Catal.* **14**, 1 (1969).