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Isomerization of 2-Pinene over Monohydrates of Metal Sulfates

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Synopsis. Catalytic activity of the monohydrates of various metal sulfates for the isomerization of 2-pinene was found to be related to the infrared wave numbers of the rocking mode of the water of crystallization and the transition temperatures from the monohydrates to the anhydrates, but not to the electronegativity of metal ions.

The catalytic activity of various metal sulfates for some acid-catalyzed reactions is related to the electronegativity of the metal ions.[1—3] The activity as well as acidity of metal sulfates is known to change a great deal with amount of water of crystallization of sulfates.[4] Since the electronegativity values of metal ions are those of bare ions independent of water molecules, they can not necessarily be correlated with the activity of metal sulfates which contain various amounts of water of crystallization. If the amount of water of crystallization is kept constant for all sulfates, a more definite relationship is expected between the electronegativity and catalytic activity. However, the effect of water of crystallization on activity has not been taken into careful consideration. We have studied the isomerization of 2-pinene over *the monohydrates* of various metal sulfates. It was found that, contrary to expectation, there is no correlation of activity with electronegativity, but good correlation between activity and the strength of the coordination of water of crystallization to metal ion.

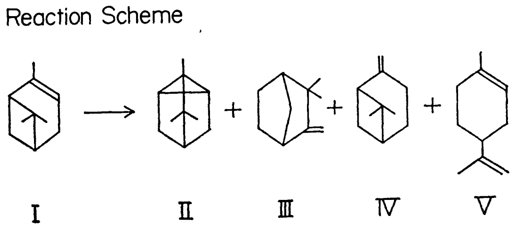
Experimental

Monohydrates of metal sulfates were prepared by first calcining the polyhydrates (guaranteed reagents, Kanto Chemical Co., except for $Cr_2(SO_4)_3\cdot4H_2O$, extra pure) at 120—130 °C, by sieving below 150 mesh after grinding to powder and then calcining for further 3 hr in air at temperatures chosen to obtain the monohydrates (Table 1). 2-Pinene was purified from turpentine oil (Wako Pure Chemical Co.) by distillation over sodium under a stream of nitrogen after separation by a preparative gas chromatograph (Perkin-Elmer F-21). All the reagents and catalysts were stored in sealed ampoules. The acidic properties of the catalysts were determined by the amine titration method with various Hammett indicators.[5] Specific surface area was obtained by applying the BET method to the adsorption isotherm of nitrogen at −196 °C.

The isomerization reaction was carried out in the temperature range 133—134 °C, except for nickel sulfate (109 °C), by stirring the reaction mixture in a cell containing 2.5—3.0 ml of 2-pinene and 0.5—1.0 g of catalysts in nitrogen atmosphere. The reaction products were analyzed by a gas chromatograph (Hitachi-Perkin-Elmer F-6D), with a 45 m capillary column of Ucon LB-550-X, after the catalyst had been removed by centrifuging.

Results and Discussion

The isomerization reaction of 2-pinene (I) gave mainly tricyclic monoterpene of 1,7,7-trimethyl-tricyclo[2.2.1.0^{2,6}] heptane (TTH, II), bicylic mono-



Scheme 1.

TABLE 1. CATALYTIC ACTIVITY[a] AND SELECTIVITY[b] OF METAL SULFATES FOR ISOMERIZATION OF 2-PINENE

Sulfates	Calcination temp. (°C)	Mole of crystal water per mol of metal	Catalytic activity $(mol\%\ min^{-1}\ g^{-1})$	Catalytic activity $(mol\%\ min^{-1}\ m^{-2})$	Selectivity	Electro-negativity[c]
Ni(II)	250	1.20	2.3	2.3×10^{-1}	0.74	9.0
Al(III)	250	1.33[d]	9.8×10^{-1}	8.2×10^{-1}	0.64	10.5
Mg(II)	250	1.10	6.0×10^{-1}	9.1×10^{-2}	0.71	6.0
Cr(III)	200	0.82[d]	4.6×10^{-1}	2.0	0.64	11.2
Co(II)	250	1.38	4.5×10^{-1}	7.4×10^{-1}	0.76	9.0
Cd(II)	150	1.02	1.2×10^{-1}	4.8×10^{-1}	0.67	8.5
Zn(II)	150	1.04	8.6×10^{-2}	3.2×10^{-1}	0.64	8.0
Ca(II)	150	0.33[d]	2.2×10^{-2}	7.9×10^{-3}	0.94[e]	5.0
Cu(II)	150	1.09	1.4×10^{-2}	1.3×10^{-2}	0.70	9.5
Mn(II)	150	1.09	8.7×10^{-3}	1.8×10^{-2}	0.73	7.5

a) Reaction temperature 133—134 °C except for 109 °C for Ni(II). b) Selectivity for formation of bicyclic monoterpenes [mol% of (II+III+IV)/mol% of I]. c) Quoted from Ref. 1. d) Monohydrates unstable. e) Unreliable because of small amount of products.

terpenes of camphene (III) and 2(10)-pinene (IV), and monocyclic monoterpene of *p*-mentha-1,8-diene (V) as shown in Scheme 1.

In order to see the selectivity of this reaction, mol% of 2-pinene remaining at reaction time *t* was plotted against mol% of camphene+TTH+2(10)-pinene or *p*-mentha-1,8-diene formed at time *t*, respectively. The plots gave straight lines in the region 100—20 mol% of 2-pinene as in nickel sulfate.[6] From the slope of the straight line, the selectivity for the formation of camphene+TTH+2(10)-pinene from 2-pinene was obtained (Table 1). The selectivity values do not vary much with the kind of sulfate.

Catalytic activity of metal sulfates expressed by initial rates per unit weight or unit surface area of catalyst is also given in Table 1. The catalysts are arranged in the order of activity per unit weight of catalyst. Either the activity per unit weight or unit surface area was found to have no correlation with the electronegativity of metal ions. The relation between activity per unit weight of catalyst and the acidic property is given in Table 2. A tendency is seen for the sulfates to have weaker acid strength or less acid amount to show less activity.

We have found that the order of activity per unit weight of catalyst agrees better with the order of the infrared wave number of rocking mode of the water of crystallization: Ni(933) > Mg(883) > Co, Cd(875) > Zn(870) > Cu(865 cm^{-1})[7] Ni(928) > Mg(889) > Co(875) > Zn(872) > Cu(865) > Mn(828 cm^{-1}).[8] This agrees also with the order of the temeratures at which the monohydrates are converted into anhydrates.[7]

Ni(420) > Mg(354) > Co, Zn(320) > Cu(270) > Mn(260) > Cd(205 °C).

The order of the temperatures and the wave numbers is considered to show the order of the bond strengths between the water of crystallization and the metal ions of the monohydrates, since, in the case of metal amine complex, Nakamoto[10] points out that the higher the NH_3 rocking frequency, the stronger the metal–nitrogen bond. The catalytic activity seems to be related with the bond strengths. The fact that the distances between the water of crystallization and the metal ions of the monohydrates measured by X-ray diffraction[9] are related to the activity supports the view:

Ni(2.0$_6$) > Zn(2.1$_5$) > Co(2.1$_7$) > Mn(2.2$_5$ Å).

However, the reason for the intensive properties such as transition temperature and wave number being correlated with the activity per unit weight and not with the activity per unit surface area has not been clarified.

Table 2. Acid property of monohydrates of metal sulfates

Catalyst	Acid amounts ($\times 10^2$ mmol/g) at various acid strengths (pK_a's)				
	−3.0	+1.5	+3.3	+4.8	+6.8
Ni(II)	4.0	6.4	6.1	6.4	—
Al(III)	0	13	—	—	—
Mg(II)	2.2	2.2	2.5	2.5	6
Co(II)	0.67[a]				
Cd(II)	0	0	0.1	0.3	0.4
Zn(II)	0.5	1.6	1.7	2.0	3
Ca(II)	0	0.2	0.3	0.7	1.4
Cu(II)	0	0.4	0.4	0.4	1.6
Mn(II)	0	0.2	0.1	0.2	0.2

a) Quoted from a paper by R. Ohnishi, S. Ishikura, and K. Tanabe, *Nippon Kagaku Kaishi*, **1973**, 183. A value at pK_a=1.00.

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