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18

CONVERSION OF POLYCHLORINATED BIPHENYLS TO USEFUL MATERIALS BY A CATALYTIC HYDROGENATION-DECHLORINATION METHOD (2)

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1. INTRODUCTION

Dechlorination of polychlorinated biphenyls (PCBs) by catalytic hydrogenation was studied, aiming at their industrial disposal and conversion into useful materials without causing any hazard to the public or the environment. High-pressure hydrogenation-dechlorination of PCBs using a Raney nickel catalyst (R-Ni catalyst) have been previously reported by us.1)2) Following these results, a series of experiments were carried out, for the most part using a carbon-supported palladium (5%) catalyst (Pd-C catalyst), under the constant near-normal pressure essential in order to take this method beyond the laboratory stage.

2 EXPERIMENT

PCB was dispersed and emulsified in a sodium hydroxide aqueous solution containing isopropyl alcohol, to react with the constant near-normal pressure of hydrogen in the presence of the Pd-C catalyst at 50° - 100°C, and was converted into biphenyl, a small amount of phenylcyclohexane and sodium chloride. This reaction was carried out using the same autoclave (capacity 50 ml) capable of oscillation as was used previously, and the temperature ring the reaction was kept constant within the change range of ±0.5°C. he details of the standard experimental conditions were also the same as for the previous occasion.1)2) The Pd-C catalyst used was 250 mg (3.3% to PCB KC-400). A constant near-normal pressure of hydrogen was supplied through a two-step controlled, highly sensitive regulator from a high pressure tank (capacity 227.5 ml) containing on average 25.0 kgw/cm^2 of hydrogen, and the pressure change was observed using a strain gauge - voltage converter within a change range of 0.01 kgw/cm^2 and an accuracy of ±0.5%, in order to estimate the hydrogen consumption during the reaction. The dechlorination ratios, the reaction products, and the amount of residual PCB were determined by the same method as was used previously.1)2)

3. RESULTS AND DISCUSSION

i) Reaction Process

As is shown in Fig. 1, it is extremely characteristic that constant pressure hydrogenation reactions using a Pd-C catalyst at 70°-100°C reveal two distinct hydrogen consumption rates, in other words are expressed as two separate straight lines. The gradient of both these lines decreases in relation to the decrease in total pressure, i.e. hydrogen partial pressure. The first straight line suggests that dechlorination occurs very rapidly, while the second line, which is almost straight, indicates a quasi-equilibrium state of dechlorination, where hydrogenation of the double bonds of biphenyl proceeds gradually, along with the slow dechlorination of residual low-chlorinated PCB.

ii) Material Balance

Certain characteristics can be seen in the material balance, as shown in Table 1, due to the controlling of hydrogen supply to the catalyst in the constant near-normal pressure reaction (hydrogen partial pressure 0.55 - 3.80 kgw/cm^2). In the reaction at 100°C, the yield of biphenyl is nearly constant at a level of 86%; phenylcyclohexane is found to depend on hydrogen pressure, and residual PCB to depend on it inversely. The yields of biphenyl were as much as 88% at 70°C, and 90% at 50°C. Very little phenylcyclohexane was produced at any temperature, due to the low hydrogen pressure. It is apparent that at the quasi-equilibrium state a slight further continuation of the dechlorination process increases the quantity of biphenyl, and the quantity of phenylcyclohexane also increases at almost the same rate; as a result, the quantity of biphenyl remains almost constant at each temperature. The material balance of the constant near-normal pressure reaction using the R-Ni catalyst is shown in Fig. 2, for comparison.

iii) Relations Between Hydrogen Pressure and Initial Dechlorination Rate

The gradients of first lines in Fig. 1 were plotted against constant reaction pressures, to produce Fig. 3. This figure clearly indicates that the reaction proceeds proportional to the first order of hydrogen partial pressure. The reaction stopped at the background pressure of the solvent 1.2 kgw/cm^2. The straight line's equation is as follows:-

$$15.0\ (x_o - 1.2) = -\frac{dx}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where x means the residual pressure of the hydrogen tank, and x_o means total reaction pressure.

iv) Activation Energy of Initial Dechlorination Reaction

The initial hydrogen consumption rate R (equivalent to the dechlorination rate) is written as follows:

$$R = -\frac{dx}{dt} = k\,P_{H_2}\,[PCB]^o = k\,P_{H_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where k corresponds to the gradient of the slope as shown in Fig. 3. The k-values at 100°C, 90°C and 70°C, under 1.00 kgw/cm^2 of hydrogen partial pressure, were studied, which gave the Arrhenius Plot shown in Fig. 4. From this gradient, the overall activation energy of the reaction was determined to be 5.5 kcal/mol. This degree of energy corresponds to the energy barrier of intermolecular force, more or less at the level of van der Waal's Force. From this result, the initial reaction rate is seen to be under the control of Henry's Law, as shown in Fig. 3, and therefore it can be inferred that the rate-determined step of the hydrogenation-dechlorination of PCB is the dissolving of hydrogen into the reaction solvent and its diffusion into the catalyst.

v) Purity of Crude Crystal Biphenyl Produced by Pd-C Catalyst

The biphenyl produced was cooled in the solution in situ at a rate of 30°C per hour; flaky biphenyl crystals were deposited. The catalyst had been filtered from the solution before it cooled. The deposit was filtered using a suction filter with ordinary filter paper, and dried in its crude state, without any purification. Crystal recovery was found to be more than 99.5%, and the residual biphenyl in the solution (95ml) amounted to less than 20mg. The crude crystal was analyzed by an ECD-gas chromatograph and found to be 99.90% pure.

REFERENCES

1) Y. Hatano, K. Nakao and T. Tomoda: Abstracts of Papers, ACS/CSJ Chemical Congress (Honolulu, Hawaii, April 1-6, 1979), Environmental Chem. Div. No.47.

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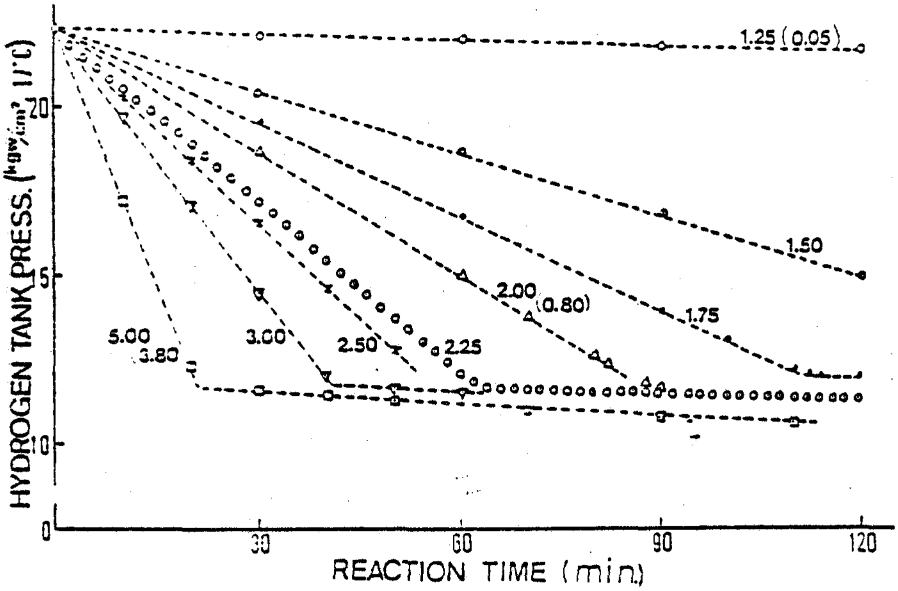

Fig. 1: Hydrogen consumption rate of constant near-normal pressure hydrogenation of PCB KC-400 by means of Pd-C Catalyst. Numbers represent total pressure (hydrogen partial pressure in brackets).

RUN NO.	TEMP. °C	TOTAL PRESS. (H₂PART. PRESS.)	TIME	HYDROGEN	DECHLORIN.	BIPHENYL Ⓐ	φ-CYCLOHEXANE Ⓑ	RESID. PCB Ⓒ	Ⓐ+Ⓑ+Ⓒ
288	100	G. 5.00 kgw/cm² ABS.(3.30)	min 120	% 92.06	% 96.87	% 85.16	% 6.98	% 1.71	% 93.85
287	100	3.00 (1.80)	120	97.08	96.54	87.03	3.00	4.81	94.84
281	100	1.75 (0.55)	120	93.64	94.38	86.25	0.16	7.79	92.71
282	90	1.55 (1.00)	90	95.01	95.98	85.40	1.37	4.91	91.68
295	70	0.71 (1.00)	150	95.69	94.53	87.79	0.16	7.14	95.09
293	50	0.28 (1.00)	165	98.21	94.46	89.21	0.07	5.99	95.20
294	50	0.83 (1.52)	160	95.35	94.02	90.69	0.12	4.31	95.12

Table 1: Material balance of constant near-normal pressure hydrogenation of KC-400 by means of Pd-C Catalyst.

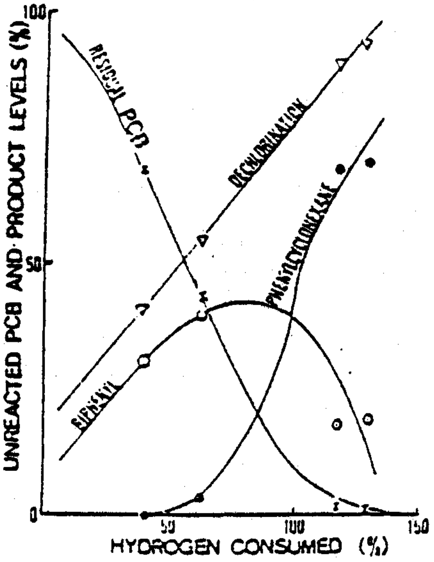

Fig. 2: Material balance of constant near-normal pressure hydrogenation of KC-400 by means of R-Ni catalyst 10°C.

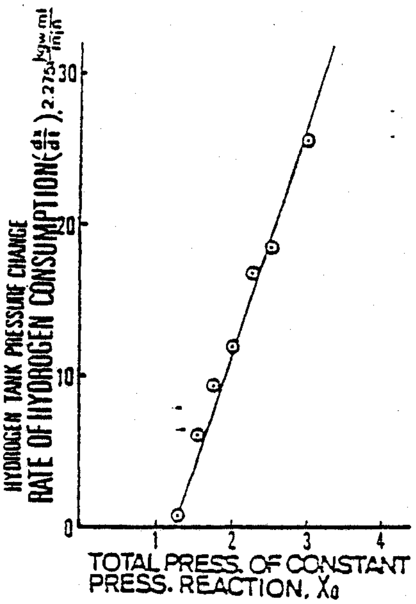

Fig.3: Relation between total pressure and reaction rate of constant near-normal pressure hydrogenation of KC-400 at 100°C.

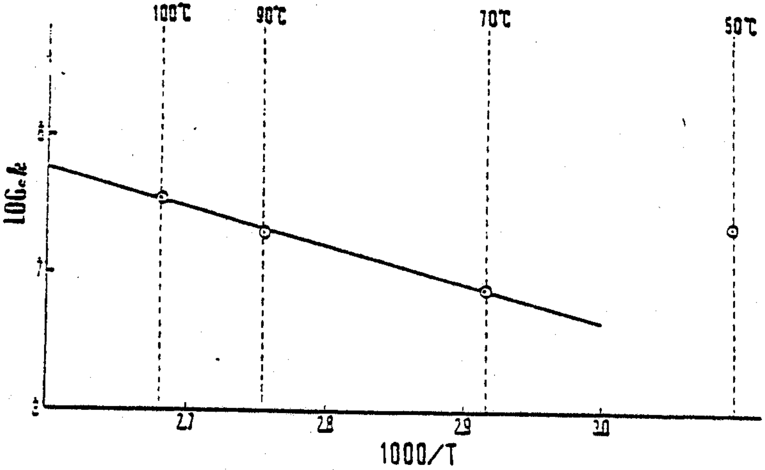

Fig. 4: Arrhenius Plot of constant near-normal pressure hydrogenation of KC-400 between 70°-100° C under hydrogen partial pressure of 1.00 kgw/cm^2.