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NOTES

A Kinetic Approach to the Problem of Reaction Yield Optimization: Isomerization of 1,5-Cyclooctadiene Catalyzed by $Ir_4(CO)_{12}/SiO_2$.

The heterogeneous catalytic isomerization of 1,5-cyclooctadiene (1,5-cod) to the 1,4- and 1,3-isomers with the aim of obtaining high yields in the intermediate 1,4-product has been the subject of some recent publications from our laboratory (*1–3*). From these studies it appears clear that Group 8 and 9 metal clusters supported on silica effectively catalyze this reaction giving good yields in the 1,4-isomer (*1, 2*).

Among these catalysts, $Ir_4(CO)_{12}/SiO_2$-based catalyst proved to be the most promising since good yields (>50%) and high selectivities (>90%) could be obtained (*2*). More recently we have undertaken a study dealing with the optimization of the system (1,4-cod yield and selectivity) with respect to the main variables involved, i.e., reaction temperature, pressure, and metal loading. For this purpose a chemometric approach (*4*) using a factorial design and surface response methods was successfully applied (*3*). In the present work the kinetic constants for the isomerization of 1,5-cod are measured and applied to the problem of optimizing the yield of 1,4-cod as desired product. It is shown that in the range of variables investigated, depending on the temperature, the yield of 1,4-cod ranges between 35 and 65%, which is much higher than the maximum yields previously reported for heterogeneous catalysts (*5*).

EXPERIMENTAL

The cluster $Ir_4(CO)_{12}$ was purchased from Strem Chemical and used as received. Solvents (C. Erba) were distilled before use and stored under nitrogen over 5A molecular sieve. 1,5-cod (EGA Chemie) was purified through a silica gel column (*6*) and stored under nitrogen over 5A molecular sieve. A highly porous silica (Grace, type 121, BET area 617 m^2/g) was used as support. The syntheses of the supported iridium carbonyls were performed as described elsewhere (*2*). Before the kinetic measurements all the catalysts were activated at 125°C for 8 h in the presence of the reaction mixture (*2*). The batch reactions were carried out under N_2 atmosphere. A typical batch experiment was carried out as follows: 0.25 ml of 1,5-cod (3.45×10^{-3} mol) were added to 15 ml of a stirred *n*-octane suspension of the supported catalyst (1 g, metal loading 1%) at the appropriate reaction temperature. No effects due to rate-limiting diffusion were observed as tested by running experiments at different stirring rates. The reaction mixture was periodically analyzed by means of GLC. The separation of the products was achieved on a 30-m-long Supelcowax 10 wide-bore (0.75 mm) column.

Flow experiments were carried in a tubular stainless-steel microflow reactor (14 cm long, 4.2-mm i.d.) interfaced to a GLC operating at atmospheric pressure and using argon as carrier and internal standard. 1,5-Cod was vaporized into the stream of the carrier by means of a thermostatted saturator. In a typical experiment 0.5 g of the activated catalyst was loaded into the reactor between two layers of granular quartz. The absence of diffusional effects was verified.

Data elaboration was performed on an IBM XT model 286 microcomputer, using readily available software: Lotus (Lotus Development Corporation) for the linear regression analysis and Surfer (Golden Soft-

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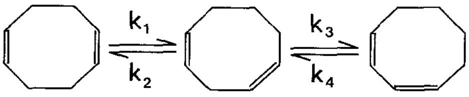
ware, Inc.) for generation and plotting of the curve reported in Fig. 2.

RESULTS AND DISCUSSION

The kinetic constants for the reaction investigated were measured using a convenient numerical method which was reported nearly 20 years ago by Himmelblau *et al.* (*7*). Since then, in spite of its potentiality, this method does not appear to be widely used by chemists. Therefore some details on the method of calculation are reported.

The proposed general scheme (*8*) for the isomerization investigated is



For this system the following differential rate equations with the boundary conditions indicated can be written

$$dX/dt = -k_1X + k_2Y \quad X(0) = 100 \qquad (1)$$

$$dY/dt = k_1X - k_2Y - k_3Y + k_4Z \quad Y(0) = 0 \qquad (2)$$

$$dZ/dt = k_3Y - k_4Z \quad Z(0) = 0, \qquad (3)$$

where X, Y, and Z are the concentrations (percentage moles) of 1.5-, 1.4-, and 1.3-cod, respectively.

The exact solutions of such differential equations (*9*) are:

$$X = 100[k_2k_4/n_2n_3 + (k_1(n_2 - k_3 - k_4)/ n_2(n_2 - n_3)) \cdot \exp(-n_2 \cdot t) + (k_1(k_3 + k_4 - n_3)/n_3(n_2 - n_3)) \cdot \exp(-n_3 \cdot t)] \qquad (4)$$

$$Y = 100[k_1k_4/n_2n_3 + (k_1(k_4 - n_2)/ n_2(n_2 - n_3) \cdot \exp(-n_2 \cdot t) + (k_1(n_3 - k_4)/ n_3(n_2 - n_3)) \cdot \exp(-n_3 \cdot t)] \qquad (5)$$

$$Z = 100[k_1k_3/n_2n_3 + (k_1k_3/n_2(n_2 - n_3)) \cdot \exp(-n_2 \cdot t) - (k_1k_3/n_3(n_2 - n_3)) \cdot \exp(-n_3 \cdot t)] \qquad (6)$$

$$n_2 = 1/2(p + q), \quad n_3 = 1/2(p - q)$$

$$p = (k_1 + k_2 + k_3 + k_4),$$

$$q = [p^2 - 4(k_1k_3 + k_2k_4 + k_1k_4)]^{0.5}.$$

An estimate of the k values can be obtained directly from the exact solutions (4)–(6) by fitting the experimental data using a nonlinear least-squares best fit procedure which, however, requires the use of large and high speed computers. Alternatively Monte Carlo methods have successfully been employed (*8*). The above problem can also be reduced to a linear least-squares regression according to the method described by Himmelblau *et al.* (*7*).

By multiplying Eqs. (1)–(3) by dt and integrating between time $t = 0$ and an arbitrary time t, the following equations are obtained:

$$X(t) - X(t_0) = -k_1 \int_0^t X dt + k_2 \int_0^t Y dt \qquad (7)$$

$$Y(t) - Y(t_0) = k_1 \int_0^t X dt - k_2 \int_0^t Y dt - k_3 \int_0^t Y dt + k_4 \int_0^t Z dt \qquad (8)$$

$$Z(t) - Z(t_0) = k_3 \int_0^t Y dt - k_4 \int_0^t Z dt \qquad (9)$$

$X(t)$, $Y(t)$, $Z(t)$ and $X(t_0)$, $Y(t_0)$, $Z(t_0)$ indicate respectively the concentrations at times t and $t = 0$ (initial concentrations). For every experimental point the integrals in Eqs. (7)–(9) can be easily evaluated from an experimental concentration vs time plot by a graphical or numerical method. Therefore they constitute new variables $I_1 - I_3$ which are used to determine the rate constants.

Keeping in mind the reaction conditions at $t = 0$, namely $X(t_0) = 100$ and $Y(t_0) = Z(t_0) = 0$, Eqs. (7)–(9) can be further simplified:

$$X(t) = 100 - k_1I_1 + k_2I_2 \qquad (11)$$

$$Y(t) = k_1I_1 - k_2I_2 - k_3I_2 + k_4I_3 \qquad (12)$$

$$Z(t) = k_3I_2 - k_4I_3 \qquad (13)$$

At this point the k values can be easily determined by solving the system of Eqs. (11)–(13)[1] for different reaction time by using multiple least-squares regression.

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[1] When n experimental points are available then the system (11)–(13) consists of 3n linear equations.

TABLE 1

Observed Rate Constants for the Isomerization of 1,5-Cyclooctadiene Associated with Statistical Error Analysis (in Parentheses)[a]

Temp (°C)	Rate constant			
	k_1	k_2	k_3	k_4
85	328(10)	127(20)	738(410)	1500(739)
100	707(14)	65(16)	557(82)	318(123)
110	1870(53)	387(29)	710(43)	190(43)
125	5958(28)	1399(94)	745(57)	192(82)

[a] Confidence coefficient 0.95, $k = 10^7$ (s^{-1}).

The kinetic constants obtained by this procedure in the range of temperatures 85–125°C together with their statistical errors are reported in Table 1.

By introducing the calculated k values into the exact solutions (4)–(6) of the differential equations (1)–(3) the calculated curves reported in Fig. 1 are obtained. The curves fit the experimental points fairly well (this is also the case for the other temperatures not reported here). This result confirms that the reaction proceeds via a kinetically controlled two-step isomerization with 1,4-cod as intermediate product (7). Moreover, *it shows the versatility of such an approach which enables one to evaluate simultaneously all the kinetic constants* k_1-k_4 *from a single catalytic run.* The small discrepancy between the calculated and observed values at the beginning of the reaction (see Fig. 1) could be related to the error in determining concentrations by GLC at low conversions.

The reaction conditions for obtaining the highest yields in 1,4-cod were found: for this the values of the observed kinetic constants reported in Table 1 were conveniently fitted by a 3rd degree polynomial function. There is no Arrhenius type dependence, since the k_i values include other contributions such as the concentration of active sites. By substituting such functions $k_i = f_i(T)$ into Eqs. (4)–(6), a new set of functions was obtained giving the yields of 1,5-cod (X), 1,4-cod (Y), and 1,3-cod (Z) within the range of reaction conditions explored. Figure 2 shows the results obtained for 1,4-cod. The curve does not show a maximum; however, the following features can be noted: (i) within the entire range of temperatures investigated, yields in 1,4-cod always exceed 35%; (ii) in order to obtain high yields (>60%) in 1,4-

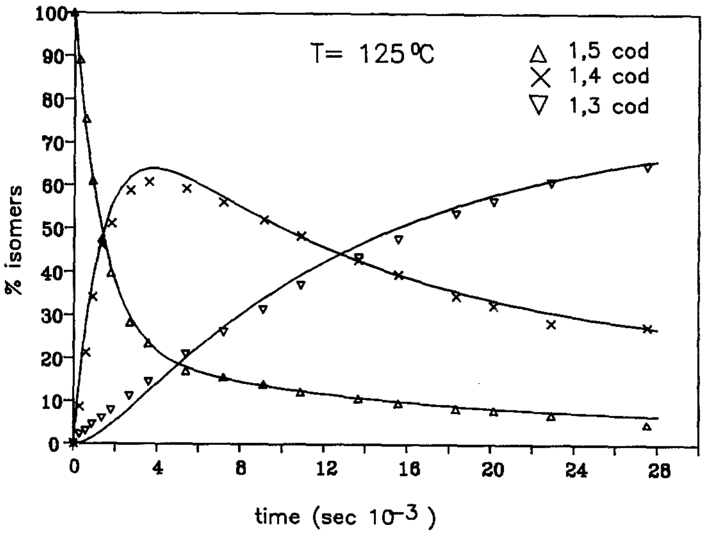

FIG. 1. Isomerization of 1,5-cyclooctadiene catalyzed by $Ir_4(CO)_{12}/SiO_2$. Comparison between the experimental points and calculated curves.

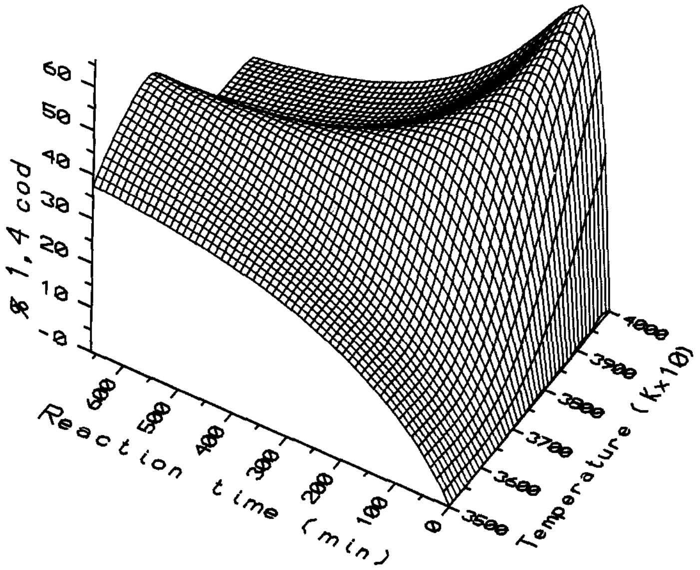

FIG. 2. Isomerization of 1,5-cyclooctadiene catalyzed by $Ir_4(CO)_{12}/SiO_2$. Yield of 1,4-cyclooctadiene vs reaction time and temperature.

cod, high temperatures and low reaction times must be used; (iii) another region of good yields (about 50%) is found at low-reaction temperatures and high-reaction times. The result of point (i) might appear somehow surprising since it has been observed that when ruthenium carbonyls are used as catalysts for this reaction, an increase in temperature leads to a decrease in 1,4-cod yield (*1*). However, it should be observed that on increasing the temperature a large increase in the k_1 values (1.5-cod disappearance) is observed (Table 1) while at the same time the k_3 values (1.4-cod disappearance) remain almost constant which accounts for the different behavior observed.

The results shown in Fig. 2 suggest that for the iridium catalyst higher temperatures favor higher yields in 1,4-cod. A set of experiments was therefore carried out in the temperature range 110–160°C. Because of the volatility of the organic reactants, these experiments have been performed in a flow reactor. The general trends observed in batch conditions are confirmed. By adoption of suitable time factor ($W/F = 129\ g_{cat}\ (g_{1,5\text{-cod}})^{-1}$ min), good yields of 1,4-cod are obtained: 60% at 110°C which is favored by an increase of the temperature (70% at 130°C). An upper temperature limit for the use of this catalyst is, however, found above 140°C, since a slow deactivation on stream is observed. $Ir_4(CO)_{12}/SiO_2$ decarbonylates above 150°C (*10*) and the metal itself is not active in this reaction (*2*).

It appears that the isomerization of 1,5-cyclooctadiene is best carried out in the range of temperatures 85–125°C and in these conditions the yields in 1,4-cod always exceed 35%. This result represents one of the best methods for obtaining 1,4-cyclooctadiene by catalytic isomerization (*5, 6*).

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