KINETICS AND MECHANISM OF THE IRON CATALYZED POSITIONAL ISOMERIZATION OF DICHLOROBUTENES

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(Received December 15th, 1970)

SUMMARY

The positional isomerization 1,4-dichloro-2-butene $\rightleftarrows$ 3,4-dichloro-1-butene is strongly catalyzed by soluble iron complexes. Kinetic data and other observations point to a mechanism involving a π-allyliron intermediate.

RESULTS AND DISCUSSION

Trans-1,4-dichloro-2-butene (1,4-DCB) isomerizes on a number of soluble transition metal catalysts to 3,4-dichloro-1-butene (3,4-DCB), as shown in Table 1. Iron catalysts have proved to be the most effective, and their activity depends only slightly on the ligands and valency state of the Fe.

Whereas the normal isomerization of olefins involves the displacement of hydrogen, the present catalysis consists in the movement of a chlorine from carbon 1 to carbon 3 or *vice versa*.
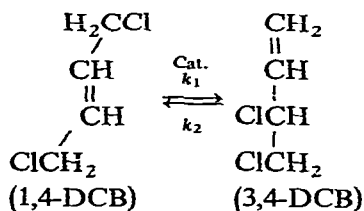
$$
\begin{array}{ccc}
\text{H}_2\text{CCl} & & \text{CH}_2 \\
\diagup & & \| \\
\text{CH} & \overset{\text{Cat.}}{\underset{k_2}{\overset{k_1}{\rightleftarrows}}} & \text{CH} \\
\| & & | \\
\text{CH} & & \text{ClCH} \\
\diagup & & | \\
\text{ClCH}_2 & & \text{ClCH}_2 \\
\text{(1,4-DCB)} & & \text{(3,4-DCB)}
\end{array}
$$

TABLE 1

ISOMERIZATION OF 1,4-DCB TO 3,4-DCB

Temp. 120°; 1 h; [Cat] $= 2 \times 10^{-3}$ mol·l⁻¹; no solvent.

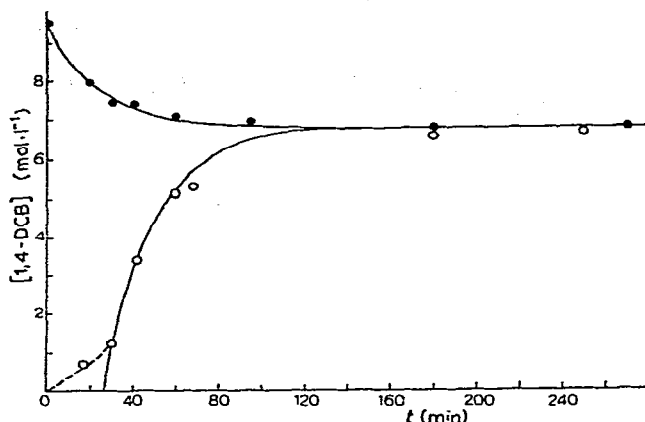| Catalyst	% 3,4-DCB	Catalyst	% 3,4-DCB
	< 1	V(Acac)$_3$	2.9
Fe(Acac)$_3$	21.4	VO(Acac)$_2$	5.7
Co(Acac)$_3$	4.0	[CpFe(CO)$_2$]$_2$	25.1
Ni(Acac)$_2$	3.4	[CpMo(CO)$_3$]$_2$	7.8
Cu(Acac)$_2$	13.5	RhCl(CO)(Ph$_3$P)$_2$	6.9
Cr(Acac)$_3$	4.7	PdCl$_2$(Ph$_3$P)$_2$	3.0

Fig. 1. The isomerization equilibrium 1,4-DCB ⇌ 3,4-DCB, starting from 1,4-DCB (upper curve) and starting from 3,4-DCB (lower curve). Solid lines: calculated with $k_1 = 0.1$ l·mole^{-1}·sec^{-1} and $k_2 = 0.26$ l·mole^{-1}·sec^{-1} [eqns. (3) and (4) resp.]. [Cat] $= 2.10^{-3}$ mole·l^{-1}; $T = 120°$.

We investigated the kinetics of this isomerization with $[CpFe(CO)_2]_2$ as catalyst (Cp = π-cyclopentadienyl). The reaction attains equilibrium at 120° after ca. 3 h. The equilibrium may be approached from either side, as shown in Fig. 1. Only very small amounts of the geometrical isomer, cis-1,4-dichloro-2-butene, were observed in the solution ($< 1\%$ at 90°, $\simeq 2\%$ at 120°, $\simeq 4\%$ at 150°, at the end of the reaction).

The rate of the positional isomerization reaction can be described by the pseudo first order rate law ([Cat] = const.):

$$-\frac{d[1,4\text{-DCB}]}{dt} = k_1 \cdot [Cat] \cdot [1,4\text{-DCB}] - k_2 \cdot [Cat] \cdot [3,4\text{-DCB}] \qquad (1)$$

This equation can be integrated, if the concentration of the 3,4-isomer is replaced by $[3,4\text{-DCB}]_t \simeq [1,4\text{-DCB}]_0 - [1,4\text{-DCB}]_t$. (This treatment neglects the small amount of the cis-isomer mentioned above). Making also use of the equilibrium constant

$$K = \frac{k_1}{k_2} = \frac{[3,4\text{-DCB}]_{\text{equil.}}}{[1,4\text{-DCB}]_{\text{equil.}}} \qquad (2)$$

one obtains:

$$k_1 = -\frac{2.3\,K}{(K+1)\cdot[Cat]\cdot t} \cdot \log_{10} \left\{ \frac{(K+1)\cdot[1,4\text{-DCB}]_t}{K \cdot [1,4\text{-DCB}]_0} - \frac{1}{K} \right\} \qquad (3)$$

If the equilibrium is approached from the 3,4-DCB side, the rate constant k_2 can be obtained:

$$k_2 = -\frac{2.3\,K}{(K+1)\cdot[Cat]\cdot t} \cdot \log_{10} \left\{ \frac{(K+1)\cdot[3,4\text{-DCB}]_t}{[3,4\text{-DCB}]_0} - K \right\} \qquad (4)$$

In Table 2, are presented the values of k_1 and k_2 calculated according to eqns. (3) and (2) (if started from 1,4-DCB) or eqns. (4) and (2) (if started from 3,4-DCB). From the consistency of the rate constants for each temperature it may be concluded that the rate expression is satisfactory. At 150° no rate constants could be measured because

TABLE 2
KINETIC DATA FOR THE ISOMERIZATION
1,4-DCB $\rightleftharpoons$ 3,4-DCB. $[DCB]_{0.20}$ = 9.5 mol·1^{-1}; no solvent.

T (°C)	K	$[Cat] \cdot 10^3$ (mole·1^{-1})	Starting isomer	t (min)	$\dfrac{[1,4\text{-DCB}]_t}{[1,4\text{-DCB}]_0}$	$\dfrac{[3,4\text{-DCB}]_t}{[3,4\text{-DCB}]_0}$	k_1	k_2
90	0.34	2.0	1,4-DCB	60	0.953		0.0071	0.021
				120	0.932		0.005	0.016
				180	0.912		0.0050	0.015
				300	0.858		0.0058	0.017
				600	0.808		0.0050	0.015
				900	0.775		0.0051	0.015
		6.0		30	0.943		0.0059	0.017
120	0.39	1.0	1,4-DCB	60	0.773		0.128	0.33
				120	0.762		0.073	0.19
		2.0		20	0.837		0.101	0.26
				30	0.783		0.112	0.29
				40	0.781		0.087	0.22
				60	0.749		0.090	0.23
		2.0	3,4-DCB	14		0.642	0.102	0.26
				32		0.457	0.103	0.26
				40		0.444	0.087	0.22
150	0.43	2.0	1,4-DCB	30–90	0.700			

the equilibrium was attained too rapidly.

As Fig. 1 shows, the isomerization of 3,4-DCB begins after a short induction period (dotted line). For the calculation of the rate constants the induction period has been neglected, as indicated by the solid line.

From the Arrhenius plot of the equilibrium constants (Fig. 2) one obtains the difference of the activation energy of the forward and backward reaction:
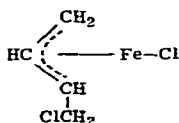
$$E_1 - E_2 = 0.65 \text{ kcal} \cdot \text{mole}^{-1}$$

This difference is of the right order of magnitude and has the sign expected from consideration of the difference between the bond dissociation energies of a carbon–chlorine bond involving primary and secondary carbon atoms[1]. Taking the average values $k_1 = 5.5 \times 10^{-3}$, $k_2 = 1.6 \times 10^{-2}$ at 90°, and $k_1 = 0.1$, $k_2 = 0.26$ at 120°, from Table 2, one obtains

$$\log_{10} k_1 \ (\text{l} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}) = 14.3 - (27{,}500/2.303 \ R \cdot T)$$
$$\log_{10} k_2 \ (\text{l} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}) = 14.4 - (26{,}900/2.303 \ R \cdot T_i)$$

A π-allyl type complex of the dichlorobutene with the iron is suggested to be the active intermediate in the positional isomerization reaction. This intermediate can be formed with 1,4-DCB as well as with 3,4-DCB by splitting of a carbon–chlorine bond:

$$
\begin{array}{c}
\text{CH}_2 \\
\diagup\!\diagup \\
\text{HC} \!\!-\!\!\!-\!\!\!-\!\!\!- \text{Fe}\!-\!\text{Cl} \\
\diagdown\cdot \\
\text{CH} \\
| \\
\text{ClCH}_2
\end{array}
\qquad (5)
$$

Presumably the chlorine atom split off remains within the complex in such a position that it can equally well attach to carbon 1 or carbon 3. The assumption of the π-allylic
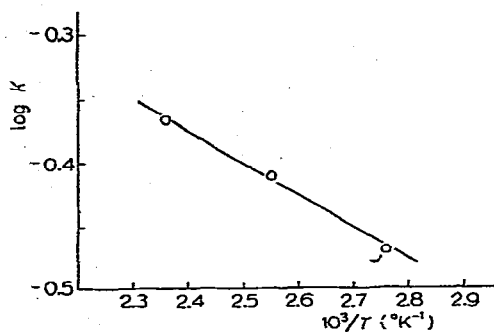
Fig. 2. Arrhenius plot of the equilibrium constant.

intermediate is supported by the fact that butadiene, which does not react with the iron catalyst alone, is polymerized in the presence of 1,4-DCB. (Compare the polymerization of butadiene with, e.g. π-allylnickel chloride[2].) The equilibration of the system then becomes feasible, since the dichlorobutene can leave the complex either as 1,4-DCB or as 3,4-DCB.
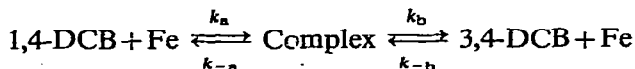
The kinetic results are in agreement with either of the following two mechanisms:

(1). Essentially all the iron is present as the π-allyl complex. The equilibration occurs via ligand displacement, according to:

$$1,4\text{-DCB} + \text{Complex} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3,4\text{-DCB} + \text{Complex}$$
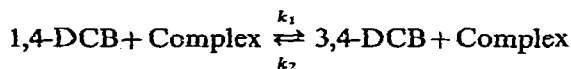
From this mechanism the rate law, eqn. (1), follows straight forwardly.

(2). Either of the two dichlorobutenes is in equilibrium with the active complex:

$$1,4\text{-DCB} + \text{Fe} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \text{Complex} \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} 3,4\text{-DCB} + \text{Fe}$$

If the concentration of the complex is small as compared with $[Fe]_0$, so that $[Fe] \simeq [Fe]_0$, and if stationary state conditions are assumed for the complex, the same formal rate law, eqn. (1) follows, with

$$k_1 = \frac{k_a \cdot k_{-b}}{k_{-a} + k_{-b}} \qquad\qquad k_2 = \frac{k_b \cdot k_{-a}}{k_{-a} + k_{-b}}$$

$$K = \frac{k_a \cdot k_{-b}}{k_b \cdot k_{-a}} = \frac{[3,4\text{-DCB}]_{equil.}}{[1,4\text{-DCB}]_{equil.}}$$

In this case the monomolecular decomposition of the complex would be the rate determining step. The relatively high activation energy of ca. 27 kcal/mole seems to favour this second mechanism.

EXPERIMENTAL

Commercial 1,4-DCB (Fluka AG, Buchs SG, Switzerland) was purified by distillation. 3,4-DCB was obtained from 1,4-DCB in a preparative isomerization run, with $[CpFe(CO)_2]_2$ as ctalyst; the lower boiling 3,4-isomer was continuously distilled off over a rectification column. Some observed physical properties of the two isomers
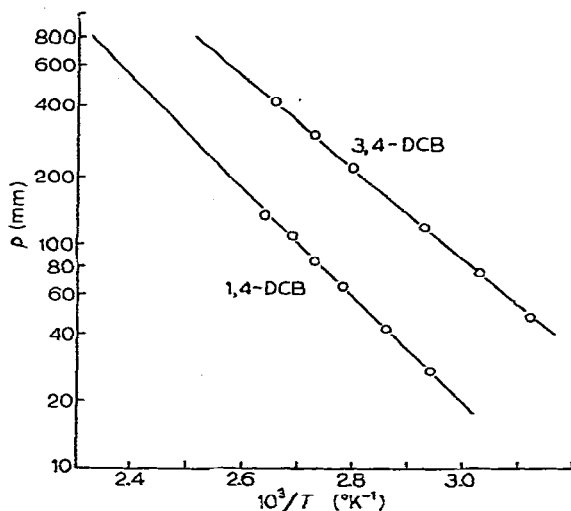
Fig. 3. Vapor pressure of the two isomers.

TABLE 3

SOME PHYSICAL PROPERTIES OF trans-1,4-DICHLORO-2-BUTENE AND 3,4-DICHLORO-1-BUTENE

Isomer	n_D^{20}	B.P. [°C(760 mm)]	Vaporization enthalpy ΔH (kcal·mole^{-1})
1,4-DCB	1.488$_9$	155	11.1
3,4-DCB	1.465$_5$	122	9.3

are given in Table 3. The vapor pressure/temperature curves are given in Fig. 3. The boiling point at 760 mm is obtained by extrapolation, and ΔH from

$$\log \frac{p_2}{p_1} = \frac{\Delta H}{2.303\,R} \left(\frac{1}{T_1}\right) - \left(\frac{1}{T_2}\right)$$

The catalyst $[CpFe(CO)_2]_2$ was supplied by Strem Chemicals Inc., Danvers, Mass. USA, all other catalysts by Fluka AG.

The kinetic data were obtained from sealed tube experiments. A weighed amount of catalyst was dissolved in the dichlorobutene contained in a glass ampoule, which was sealed off after degassing. After the appropriate time, the mixture of dichlorobutenes was separated from the catalyst by vacuum distillation. The composition of the mixture was determined by gas-chromatography, on a Perkin–Elmer F 900 instrument (polyethylene-glycol column, 120°, hot wire detection).

REFERENCES

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2 G. WILKE, B. BOGDANOVIC, P. HARDT, P. HEIMBACH, W. KEIM, M. KRÖNER, W. OBERKIRCH, K. TANAKA, E. STEINRÜCKE, D. WALTER AND H. ZIMMERMANN, Angew. Chem., 78 (1966) 157.