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The Carbon Dioxide-Catalyzed Ester Exchange Reaction

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Carbon dioxide has long been recognized as an inert gas for most neutral organic compounds. However, we have reported in a previous communication[1] that, contrary to the above view, CO_2 catalyzes the transacylation reaction from acid amides to amines. We now wish to report that CO_2 can also catalyze the ester-exchange reaction between carboxylic esters and alcohols.

Results and Discussion

A solution of butyl formate in an excess of ethanol was agitated by a stream of dry CO_2 at room temperature for 5 hr. The vpc analysis of the reaction mixture revealed that this simple treatment gave rise to an ester-exchange reaction affording ethyl formate in a 30% yield. A similar exchange reaction was also observed between other carboxylic esters and alcohols. The results are summarized in Table 1.

$$RCO_2R' + R''OH \xrightarrow{CO_2} RCO_2R'' + R'OH$$

In the controlled experiments, mixtures of butyl formate and *n*-octyl alcohol and of ethyl butyrate and butyl alcohol were allowed to stand, or were agitated by a stream of N_2, for 5 hr at room temperature. No exchange reaction was observed in any of these treatments, confirming that CO_2 must be a catalyst for the reaction.

The ester-exchange reaction was also conducted in an autoclave under the pressure of CO_2. The results are summarized in Table 2. The controlled experiments, which were carried out under the pressure of N_2, confirmed that the exchange reaction is always CO_2-catalyzed reaction, except for the reaction of butyl formate at elevated temperatures (see runs 14 and 18). The reason for this exception was clarified

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[1] Y. Otsuji, N. Matsumura, and E. Imoto, This Bulletin, **41**, 1485 (1968).

Table 1. The ester exchange reaction in a stream of CO_2[a]

	Ester	Alcohol	Temp., °C[b]	Product	
				Compd.	Yield, %
1	$HCO_2C_4H_9$	C_2H_5OH	rt	$HCO_2C_2H_5$	30
2	$HCO_2C_4H_9$	$C_6H_{11}OH$	rt	$HCO_2C_6H_{11}$	10
3	$HCO_2C_4H_9$	$(CH_3)_3COH$	rt	no reaction	0
4	$HCO_2C_4H_9$	n-$C_8H_{17}OH$	0	$HCO_2C_8H_{17}$	35
5	$HCO_2C_4H_9$	n-$C_8H_{17}OH$	rt	$HCO_2C_8H_{17}$	27
6	$HCO_2C_4H_9$	n-$C_8H_{17}OH$	50—60	$HCO_2C_8H_{17}$	10
7	n-$C_3H_7CO_2C_2H_5$	n-C_4H_9OH	0	$C_3H_7CO_2C_4H_9$	27
8	n-$C_3H_7CO_2C_2H_5$	n-C_4H_9OH	rt	$C_3H_7CO_2C_4H_9$	20
9	n-$C_3H_7CO_2C_2H_5$	n-C_4H_9OH	50—60	$C_3H_7CO_2C_4H_9$	4
10	$C_6H_5CO_2C_2H_5$	n-C_4H_9OH	rt	no reaction	0

a) The reaction time was 5 hr.
b) The "rt" indicates the room temperature, which was ~20°C.

Table 2. The ester exchange reaction under the pressure of CO_2

	Ester	Alcohol	Reaction conditions			Product	
			Temp., °C[a]	Time, hr	Press, kg/cm	Compd.	Yield, %
11	$HCO_2C_4H_9$	n-$C_8H_{17}OH$	rt	5	50	$HCO_2C_8H_{17}$	5
12	$HCO_2C_4H_9$	n-$C_8H_{17}OH$	rt	12	50	$HCO_2C_8H_{17}$	13
13	$HCO_2C_4H_9$	n-$C_8H_{17}OH$	rt	30	50	$HCO_2C_8H_{17}$	29
14	$HCO_2C_4H_9$	n-$C_8H_{17}OH$	100—110	5	150	$HCO_2C_8H_{17}$	27
15	n-$C_3H_7CO_2C_2H_5$	n-C_4H_9OH	100—110	5	150	$C_3H_7CO_2C_4H_9$	Trace
16	$C_6H_5CO_2C_2H_5$	n-C_4H_9OH	100—110	5	150	no reaction	0
			Controlled experiments[b]				
17	$HCO_2C_4H_9$	n-$C_8H_{17}OH$	rt	5	50	no reaction	0
18	$HCO_2C_4H_9$	n-$C_8H_{17}OH$	100—110	5	50	$HCO_2C_8H_{17}$	52
19	n-$C_3H_7CO_2C_2H_5$	n-C_4H_9OH	100—110	5	50	$C_3H_7CO_2C_4H_9$	Trace

a) The "rt" indicates the room temperature, which was ~20°C.
b) The controlled experiments were conducted under the pressure of N_2.

when the reaction products were carefully analyzed. The vpc analysis of the reaction mixture obtained after the treatment of butyl formate with octyl alcohol under the pressure of N_2 at 100—110°C showed that the mixture contained formic acid and butene-1. Both products could be formed by the thermal decomposition of butyl formate. The formic acid thus produced would react with octyl alcohol to give octyl formate. The formation of the ester from formic acid under the experimental conditions was in fact verified by a separate experiment.

$$HCO_2C_4H_9 \xrightarrow{\Delta} HCO_2H + CH_3CH_2CH{=}CH_2$$

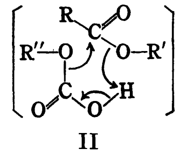
$$HCO_2H + n\text{-}C_8H_{17}OH \rightarrow HCO_2C_8H_{17}$$

Thus, the striking features of this study can be summarized by the following four items; (i) the reactivities of esters decrease in the order of; butyl formate > ethyl butyrate > ethyl benzoate (runs 5, 8, and 10), implying that the increase in the positive charge on the carbonyl carbon of the esters makes the progress of the reaction profitable; (ii) the reactivities of the alcohols decrease in the order of; primary > secondary tertiary > (runs 1, 2, 3, and 5); (iii) the yield of the exchanged esters increases with the decrease in the reaction temperature (runs 4, 5; and 6, 7, 8, and 9); and (iv) the increase in the reaction time increases the yield of the exchanged esters (runs 11, 12, and 13).

On the basis of these observations, together with those described in the previous paper,[1] we tentatively propose the mechanism shown in Scheme 1 for the ester-exchange reaction:

$$R''OH + CO_2 \rightleftharpoons \underset{\textbf{I}}{R''OCO_2H} \qquad (1)$$

$$\textbf{I} + RCO_2R' \rightarrow \qquad (2)$$



II

$$\textbf{II} \rightarrow RCO_2R'' + R'OH + CO_2 \qquad (3)$$

Scheme 1

The reversible reaction (1) has been postulated by Hempel and Seidel,[2] mainly on the basis of the freez-

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[2] W. Hempel and J. Seidel, *Ber.*, **31**, 2997 (1898).

ing-point elevation of an alcohol containing CO_2 and the molecular composition of the isolated product. However, the equilibrium constant for this reaction has not yet been determined. Nevertheless, it is reasonable to assume that the equilibrium constant for the reaction (1) in various alcohols is proportional to the solubility of CO_2 in the alcohols. The solubility data[3] of CO_2 in alcohols suggest that the equilibrium constants would decrease in the order of; primary> secondary>tertiary alcohols, an order which is in accordance with the reactivity order of the alcohols for the ester-exchange reaction. This fact and the effect of the temperature on the yield of the exchanged esters are consistent with the assumptions that reaction (1) is involved in the initial stage of the reaction and that the monoalkyl carbonate (I) is a reactive species; the concentration of I would increase with a lowering of the temperature by means of the increase in the solubility of CO_2; and accordingly, the yield of the exchanged esters would increase with a lowering of the temperature.

The monoalkyl carbonate I would then react with an ester to form a six-membered transition state (II), which would spontaneously collapse to give the exchanged ester, accompanied by the elimination of the alcohol (R'OH) and CO_2. At this stage, the nucleophilic reactivity of the alcohol may be enhanced to some extent, since the temporary formation of an alkoxide ion ($R''O^-$) would be expected at the moment of the elimination of CO_2.

Experimental

The vpc analyses were preformed with a Yanagimoto GCG-5DH gas chromatograph, employing a stainless steel column (1.5 m × 3 mm o.d.) packed with 30% PEG-20 M on Chromosorb (80 mesh) and using helium as the carrier gas. For quantitative analyses, the respective authentic samples were used as the internal standards.

All the compounds used were purchased or prepared by the standard methods, and they were purified by distillation before use. CO_2 was generated from dry ice and was dried by passing it through concentrated H_2SO_4 and then a column packed with $CaCl_2$.

Ester-exchange Reaction in a Stream of CO_2. A solution of an ester (~0.05 mol) in an alcohol (0.1—0.2 mol) was placed in a flask equipped with a gas inlet and outlet tubes, to which a tube packed with $CaCl_2$ was connected. Dry CO_2 was then passed into the solution. The passing rate was so adjusted as to maintain the rate as constant as possible throughout the whole series of experimental runs. After an appropriate period of time, an aliquot taken up from the reaction mixture was subjected to vpc analysis.

Control experiments were carried out under conditions similar to those employed above except that the passing gas was changed from CO_2 to N_2. In these experiments, the exchanged esters were not obtained in a detectable yield, but the starting materials were recovered.

Ester-exchange Reaction under the Pressure of CO_2. To a solution of an ester (~0.03 mol) in an alcohol (0.1—0.2 mol) placed in a 300-m*l* autoclave, we added small pieces of dry ice. The autoclave was then closed and warmed to the reaction temperature. After checking the pressure, the autoclave was shaken for an appropriate period of time. An aliquot was pipetted out from the reaction mixture and then subjected to vpc analysis.

Control experiments were carried out under conditions similar to those employed above except that N_2 was used in place of CO_2.

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[3] H. Stephen and T. Stephen, "Solubilities of Inorganic and Organic Compounds," Vol. 1, Pergamon Press, Oxford, London (1963), pp. 1058—1076.