Triethylamine as an effective catalyst for the reaction of CO_2 with epichlorohydrin

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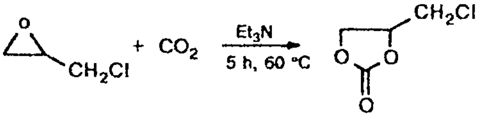
Tertiary amines were shown to catalyze efficiently the reaction of CO_2 with epichlorohydrin at 60 °C and atmospheric pressure.

Key words: carbon dioxide, epichlorohydrin, triethylamine, cyclic carbonates.

Interest in the development of chemical methods for binding carbon dioxide has increased considerably in recent time. This is related, on the one hand, to the problem of the greenhouse effect due to the accumulation of CO_2 in the atmosphere and, on the other hand, to the cheapness and accessibility of carbon dioxide as the C(1) synthon.[1,2] Binding of CO_2 in reactions of epoxides affording alkylene carbonates is considered to be very promising, since polycarbonates obtained from alkylene carbonates are valuable chemical products.[3] In addition, unlike the transformation of CO_2 into the fuel by hydrogenation, binding of CO_2 into polymers removes it for a long time from the natural cycle.

Inorganic salts and bases, quaternary ammonium salts, and tertiary amines are used as catalysts in reactions of alkene oxides with carbon dioxide.[3] It was also shown that tertiary amines did not catalyze the reaction of CO_2 with propylene oxide that has underwent thorough purification. The reaction occurred only in the case where technical-grade propylene oxide was used as the starting raw material. This is explained by the fact that tertiary amines react, under the reaction conditions, with admixtures of organochlorine compounds present in technical-grade propylene oxide to form quaternary ammonium salts, which catalyze the process.[3]



Assuming that quaternary ammonium salts are formed *in situ* in the reaction of epichlorohydrin with CO_2 in the presence of organic bases, we studied this reaction in the presence of catalytic amounts of different amines (Table 1) and found that triethylamine was the most convenient catalyst.

The reactions of epichlorohydrin with CO_2 in the presence of triethylamine were previously performed[4] at 180—200 °C and 50—100 atm with a yield of the product of 97—98%.

Table 1. Different organic bases as catalysts in the reaction of CO_2 with epichlorohydrin

Base	T/°C	Duration /h	Molar ratio (epichlorohydrin /base)	Yield of chloromethylethylene carbonate (%)
Pyridine	70	6	5.14	58.5
Pyridine	60	6	5.14	21.6
Pyridine	50	6	5.14	10.9
Diethylaniline	70	6	5.14	1.06
N-Methylimidazole	70	6	5.14	28.8
Quinoline	70	6	5.14	7.5
Triethylamine	70	6	5.14	36.6
Triethylamine	60	6	5.14	100.0
Triethylamine	60	5	5.14	75.5
Triethylamine	60	5	6.0	99.4
Triethylamine	60	5	7.0	60.0

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Experimental

IR, NMR, and mass spectra were recorded on Bruker IFS-113, Bruker CXP-200, and Finnigan GS/MS-4021 instruments, respectively.

Epichlorohydrin (2.36 g, 0.0257 mol) and triethylamine (0.43 g, 0.0043 mol) were placed in a jacketed three-neck flask flushed with carbon dioxide. The flask was equipped with a reflux condenser with a rubber balloon filled with an excess of CO_2. The reaction mixture was heated at 60 °C in the atmosphere of CO_2 and stirred for 5 h. After distillation of the reaction mixture, chloromethylethylene carbonate (3.39 g, 99.4%) with b.p. 145—148 °C (10 Torr) was obtained. IR (CH_2Cl_2), ν/cm^{-1}: 1817—1818 (C=O). ^1H NMR (200 MHz, $CDCl_3$, Me_4Si), δ: 3.75 (m, 2 H, OCH_2); 4.36 (m, 1 H, CHCl); 4.56 (m, 1 H, CHCl); 5.00 (m, 1 H, OCH). ^{13}C NMR (50.3 MHz, $CDCl_3$, Me_4Si), δ: 44.1 (t, CH_2Cl); 66.8 (t, OCH_2); 74.4 (d, OCH); 154.4 (s, C=O). MS (EI, 70 eV), *m/z* : 136, 138 $[M]^+$.

Reactions with other bases used as catalysts were performed according to the same procedure. The yields of the product were determined without its isolation, by IR spectroscopy using a calibration line.

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Action of gaseous ammonia and water on neodymium diphthalocyanine

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The method of flow injection into the gas flow with detection of current resistance of the film was used to investigate the action of ammonia and water vapor on neodymium diphthalocyanine film. The value and sign of the electrophysical response are reversible at 18—22 °C. When the film contacts with vapor, the current is changed within a few seconds, whereas the relaxation to the initial value when vapor is removed occurs within tens of seconds. The response parameters are suitable for developing effective sensors based on resistant films. No optical changes in the absorption spectra of the films were observed in the 400—800 nm region under the action of ammonia and water vapor.

Key words: phthalocyanine, neodymium; conductivity; ammonia, water, gas.

Metallophthalocyanines[1] can be used as gas-sensitive films toward ammonia vapor.[2,3] We have recently obtained metallodiphthalocyanines of rare-earth elements (REE), actinides, hafnium, and zirconium.[4] Films of these sandwich-type compounds were shown to be sensitive to the action of both strong electron donors (metallic sodium vapor[5]) and acceptors (NO_2 and I_2 vapor[6,7]). In this work, we studied the gas sensitivity of neodymium diphthalocyanine films $PcNdPc^{\cdot}$ (where $Pc^{\cdot} = (C_{32}H_{16}N_8)^{1-}$, $Pc = (C_{32}H_{16}N_8)^{2-}$) to the action of vapor of relatively weak electron donors and acceptors such as ammonia and water. Compared to other metallophthalocyanines, these compounds show lower activation energies of conductivity, different patterns of

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