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Preparation and Properties of the Alkylene Carbonates

In addition to their applications in synthesis, the alkylene carbonates are highly polar solvents, particularly useful for obtaining solutions of organic polymers. They can be made by a relatively simple manufacturing process, but special catalysts are needed

THE alkylene carbonates, or 1,2-glycol carbonates, can be expected to attract increased attention, as they not only possess a number of unusual properties but can be made by a relatively simple manufacturing process. Historically, ethylene carbonate, the simplest of these cyclic esters, has been made from ethylene glycol and phosgene (*14*), from diethyl carbonate and ethylene glycol by trans-esterification (*13*), and from ethylene chlorohydrin and sodium bicarbonate (*16*). These reactions have seen little practical application. In 1943, a German patent disclosed that the alkylene carbonates could be prepared readily from the corresponding 1,2-epoxides and carbon dioxide (*18*).

Despite the considerable interest that the new reaction held for the author's laboratory, low yields were generally obtained with the catalyst described. Essentially a composition involving sodium hydroxide carried on activated charcoal as a support, the catalyst was short-lived. There was reason to conclude that the catalyst became inactive through conversion of the alkali hydroxide to carbonate or bicarbonate, neither of which was an effective catalyst. Water retained by the catalyst may have initiated undesirable side reactions involving the ethylene oxide. Without exception a considerable amount of high-boiling, water-soluble coproduct was obtained in all runs. This reasoning stimulated a search for other catalysts.

Quaternary ammonium halides were remarkably active and their use enabled virtually quantitative yields of alkylene carbonates to be obtained (*12*). Recent patents disclose that tertiary amines or quaternary ammonium bases (*7*) and calcium or magnesium halides (*5*) can also be used with good results. Ethylene carbonate and propylene carbonate are now sold commercially and hold promise of becoming available at low price, should substantial uses be found.

The preparation of ethylene carbonate is more or less typical. The reaction of ethylene oxide with carbon dioxide is initiated by the quaternary ammonium halide at about 150° to 175° C. An excess of carbon dioxide is desirable, to ensure substantially complete conversion of ethylene oxide. Carrying out the reaction accordingly requires use of a vessel able to withstand a working pressure of 1000 to 1500 p.s.i.g. Because the reaction is rapid and no side or secondary reactions are involved, the removal of the 23 kcal. per gram mole of heat liberated is the most important consideration governing the setting of a holding time.

A considerable number of quaternary ammonium halides can serve as catalysts, solubility in the reaction mixture being the important requirement. Tetraethylammonium bromide is particularly easy to prepare and the required intermediates are available commercially. The quaternary salt can be prepared in the desired alkylene carbonate as a solvent when available.

Equimolar amounts of triethylamine and ethyl bromide are mixed with the alkylene carbonate in proportions to give a 10 to 15% solution of catalyst. The mixture is heated to 80° to 100° C. for 2 hours in a closed vessel capable of withstanding the 15- to 20-pound pressure generated, and when cooled is ready for use. About 0.25 to 0.5% of catalyst based upon the weight of alkylene oxide and carbon dioxide is ordinarily sufficient to maintain a rapid reaction. The catalyst can be recovered for re-use.

Operation of a Pilot Plant

A continuous reactor assembly for the preparation of the alkylene carbonates is illustrated in the diagram. A prototype was constructed and operated successfully in a pilot plant study of the reaction.

Thermocouples placed as shown were connected to a multipoint recorder.

Ethylene oxide or propylene oxide was introduced from storage by a positive dual-action displacement pump.

Pilot Plant Equipment

Vessels and lines	Carbon steel
Reactor	8-inch Schedule 160 seamless pipe, 4 feet long, working vol. 1 cu. foot
Mixing zone	6-inch depth of ceramic rings at grid near top
Finishing drum	Pressure vessel, 1/2 vol. of reactor
Cooler and reheater	Shell- and tube-type exchangers, area of approx. 7.5 sq. feet, heated by controlled steam pressure
Still	Glass-lined batch, Pfaudler Co., Rochester, N. Y.
Gas-liquid separator	Light construction
Pumps	
Positive dual-action displacement	0- to 60-gal./hour capacity at 3000 p.s.i.g., Texsteam Corp., 322 Hughes St., Houston, Tex.
Positive displacement duplex	0- to 5-gal./hour at 3000 p.s.i.g., Cardox Corp., 305 North Michigan Ave., Chicago, Ill.
High pressure service gear, for mixing	20 gal./min., Northern Pump Co., Minneapolis, Minn.

Table I. Operation of Pilot Plant for Alkylene Carbonates

	Ethylene Carbonate		Propylene Carbonate,
	Run 1	Run 2	Run 3
Reactor			
Alkylene oxide, lb./hr.	75	150	100
Carbon dioxide, lb./hr.	80	160	80
TEAB[a], lb./hr.	0.4	1.6	0.5
Alkylene carbonate, lb./hr.	2.6	10.4	3.5
Catalyst solution, lb./hr.	3.0	12.0	4.0
Reactor conditions			
Catalyst feed, ° C.	100	100	100
Alkylene oxide feed, ° C.	30	30	30
Carbon dioxide feed, ° C.	40	40	40
Reactor top, ° C.	155	152	150
Reactor mid, ° C.	180	183	172
Reactor bottom, ° C.	195	197	185
Reheater outlet, ° C.	160	157	160
Cooler outlet, ° C.	50	55	50
Finishing drum, ° C.	180	185	180
Reactor pressure, p.s.i.g.	1500	1500	1500
Av. holding time, reactor, min.	38	19	32
Av. holding time, finishing drum, min.	14	7	12
Total av. holding time, min.	52	26	44
Reactor effluent			
TEAB[a], lb./hr.	0.4	1.6	0.5
Crude carbonate, lb./hr.[b]	148.6	300.4	171.0
Total crude, lb./hr.	149.0	302.0	171.5
Unreacted alkylene oxide, lb./hr.	1.5	4.0	3.0
Unreacted carbon dioxide, lb./hr.	6.5	14.0	8.0
Total vent gas, lb./hr.	8.0	18.0	11.0
Loss, lb./hr.	1.0	2.0	1.5

[a] Tetraethylammonium bromide.

[b] Found 99.0% pure by distillation analysis.

Table II. Physical Properties of Ethylene Carbonate and Propylene Carbonate

	Ethylene Carbonate	Propylene Carbonate
Melting point, ° C.	36.4	−49.2
Boiling point, ° C. (760 mm.)	248	241.7
Specific gravity	1.3218 (39/4° C.)	1.2057 (20/4° C.)
Refractive index, n_D	1.4158 (40° C.)	1.4209 (20° C.)
Heat of vaporization, cal./mole	13,500 (150° C.)	13,200 (150° C.)
Specific heat, cal./g., 50° C.	0.363	0.431
Dielectric constant, e.s.u.	69.0 (25° C.)	69.0 (23° C.)

The catalyst solution pump was a positive-displacement duplex pump. Carbon dioxide was supplied from a Cardox storage unit at 40° C. and delivered to the reactor by a compressor set at 1500 p.s.i.g., the reactor accordingly being charged with gas to the latter pressure. The holding time in the reactor could be varied from 20 to 60 minutes by adjusting the alkylene oxide and catalyst solution feed rates. Mixing was obtained by a high-pressure-service gear pump.

The product was let down to 5 p.s.i.g. pressure at the gas-liquid separator, where the bulk of the excess carbon dioxide was vented. The small additional amount of dissolved carbon dioxide, with some unreacted ethylene oxide, was released from the product in crude storage.

The crude product was distilled in a glass-lined batch still having a short column section serving mainly for elimination of entrainment. Steam supplied to the jacket at 50 p.s.i.g. was the source of heat and the distillation rate was controlled by regulating the vacuum. With the head pressure at 3 to 5 mm. the ethylene carbonate distilled at about 110° C.

When the quaternary ammonium halide catalysts are used, the crude product is relatively stable and can be distilled without prior separation of the catalyst. Distillation under reduced pressure, 50 mm. or less, is desirable to ensure good product quality. Generally, no low-boiling forerun is encountered and colorless ethylene carbonate, freezing at 36° C., can be taken directly overhead. Catalyst is recovered for re-use by not continuing the distillation beyond a 90 to 95% recovery of product. The distillation residue may be used directly, but it is desirable to discard about 30% and make up the additional requirement with fresh catalyst.

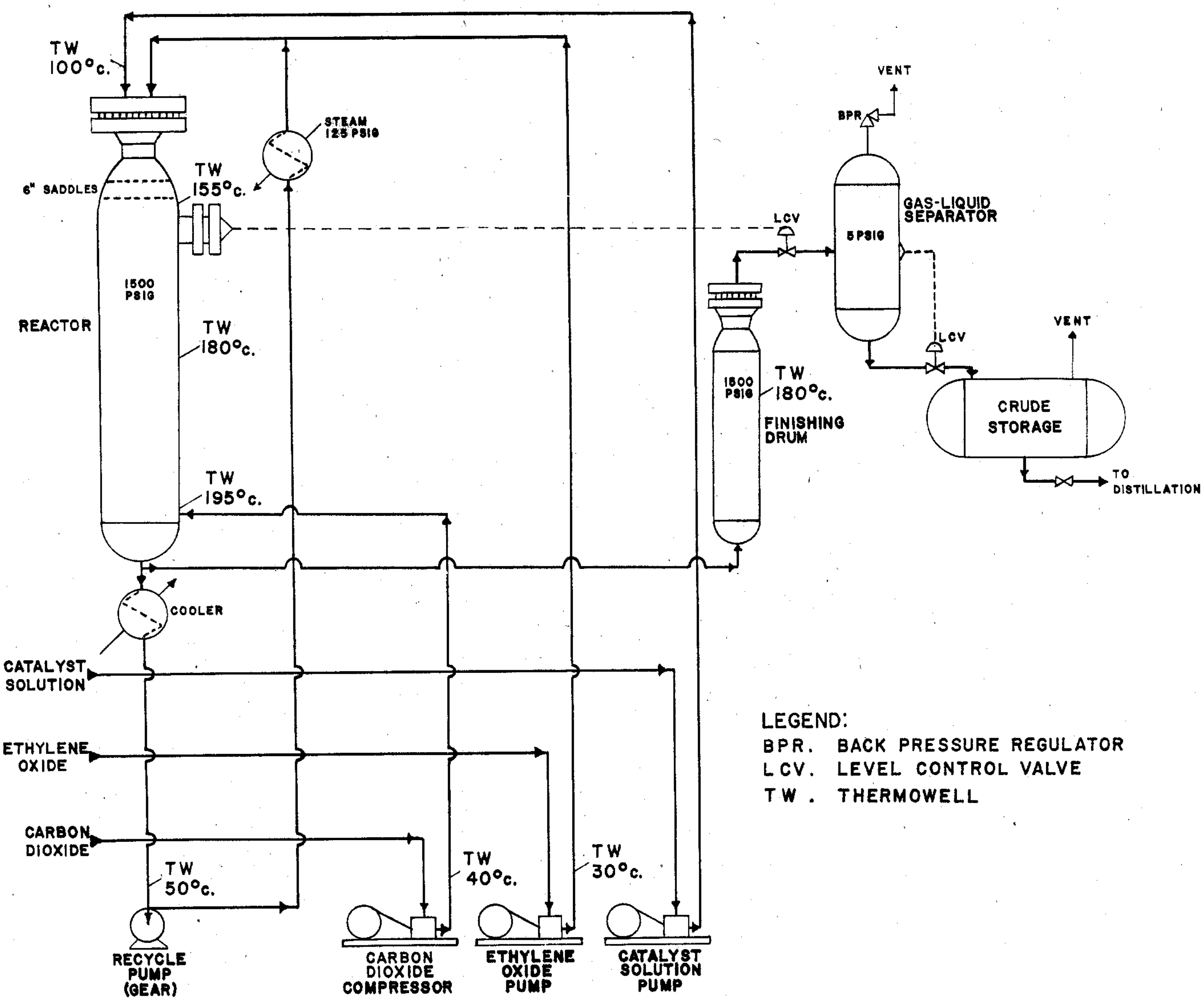
Data selected from several typical runs are summarized in Table I.

Scope of Alkylene Carbonate Synthesis from Epoxides

Cyclic carbonates have been prepared from a variety of 1,2-epoxides in addition to ethylene oxide and propylene oxide. Isobutylene oxide, cyclohexene oxide, styrene oxide, and epichlorohydrin react smoothly with carbon dioxide when a quaternary ammonium halide is the catalyst (*9*). Surprisingly, 2,3-butylene oxide as an approximately equal mixture of the cis and trans forms did not react under the conditions used generally for the other epoxides.

Properties of Alkylene Carbonates

Ethylene carbonate is a low melting solid. Propylene carbonate is a liquid that can only with difficulty be induced



This pilot plant was operated successfully to study production of alkylene carbonates

to congeal at about −50° C. Other selected physical properties of the pure esters are given in Table II.

Pure ethylene and propylene carbonates are relatively stable at elevated temperatures. Technical ethylene carbonate, if distilled rapidly at atmospheric pressure, can be recovered almost unchanged. However, many substances, particularly those having active hydrogen, react readily with ethylene carbonate and the reactions may be catalyzed by acids or bases. Other substances can accelerate a thermal decomposition of the ester, with evolution of both carbon dioxide and ethylene oxide. Metal oxides, silica gel, and activated carbon are active at 200° C. (*2*). In this laboratory tetraethylammonium bromide itself catalyzed the breakdown of ethylene carbonate at elevated temperatures. Lithium chloride, however, was a more efficient catalyst; a 1% solution in ethylene carbonate gave an estimated 65% yield of ethylene oxide at 175° C. in 2 hours. The ethylene oxide was collected by passing the evolved gas from the decomposition through suitable water scrubbers and estimating the amount by epoxide analysis. In the ordinary handling of the alkylene carbonates, distillation can usually be carried out without difficulty under reduced pressure, if near-neutrality is maintained.

Hydrolysis of ethylene carbonate is accelerated greatly by bases and to a much lesser extent by acids. As shown in Table III, propylene carbonate is appreciably more resistant to hydrolysis than ethylene carbonate. Hydrolysis was followed by measuring the evolved carbon dioxide with respect to time.

Technical ethylene carbonate may contain a small amount of ethylene glycol, often a troublesome contaminant in recovered ethylene carbonate. Separation by distillation is complicated by the existence of an azeotrope boiling lower than ethylene carbonate. The composition of this azeotrope at several different pressures is given in Table IV. Distillation under only moderately reduced pressure is advantageous. The purity of ethylene carbonate can be assayed with satisfactory precision by saponifying a sample with 1.0*N* sodium hydroxide and titrating the unreacted

Table III. Hydrolysis of Alkylene Carbonates

(One mole of aqueous solutions at 100° C.)

Catalyst	Wt. %	Reaction Rate Constant[a] Ethylene carbonate	Reaction Rate Constant[a] Propylene carbonate
Na_2CO_3	0.05	183.0	139.0
H_2SO_4	0.25	18.0	13.0
None		5.9	3.9

[a] Mole liters^{-1} sec.$^{-1}$ × 10^6.

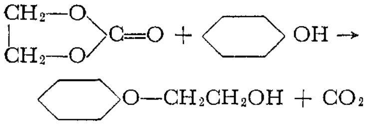
alkali with standard acid to an end point of pH 9.

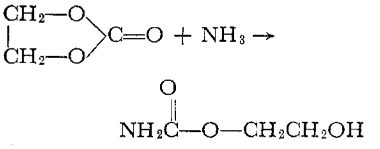
Table IV. Azeotrope of Ethylene Glycol and Ethylene Carbonate

Pressure, Mm.	B.P., ° C.	Ethylene Glycol, Wt. %
10	88	13.9
25	107	7.5
50	122	2.6
72	163	0

Reactions of Alkylene Carbonates

The ability of ethylene carbonate to undergo alkyl-oxygen cleavage can be utilized to obtain the same hydroxyethyl derivatives of many substances as with ethylene oxide. Phenols and thiophenols in particular react smoothly with ethylene carbonate and hydroxyethyl derivatives are obtained in high yields (*4*). The reaction is easily brought about by heating the reactants at 100° to 150° C. with a small amount of alkaline catalyst. Ammonia, aliphatic amines generally, and many secondary amines react at relatively low temperatures, yielding carbamates (*17*). On the other hand, when an amine is low in basicity and a fairly high temperature is needed to initiate reaction—e.g., aniline—hydroxyethylation of the amino nitrogen occurs (*10*).


(1)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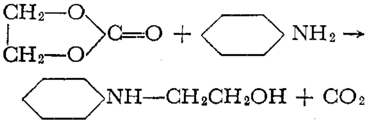
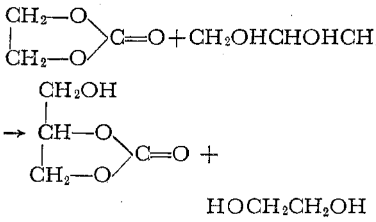
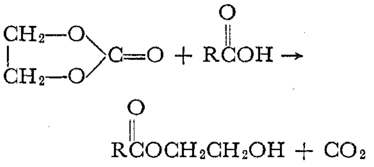

(3)

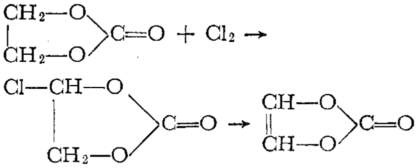
Similarly, the reaction of ethylene carbonate with aliphatic alcohols may follow two courses. Heating the reactants to 150° C. with an alkaline catalyst results in evolution of carbon dioxide with hydroxyethylation, but in this laboratory the products were usually complex. At lower temperatures, 100° to 125° C., particularly if a mildly acidic or alkaline catalyst is employed, reaction can be substantially limited to simple ester interchange. Where an alcohol appreciably less volatile than ethylene glycol is involved, the latter can be eliminated by distillation and the exchange forced to completion. A glyceryl carbonate reported to be largely polymeric was prepared by Bruson from glycerol by ester interchange with ethylene carbonate and shown to undergo pyrolysis to the epoxide, glycidol, in good yield (*3*). If the ester interchange is carried out carefully, a monomeric glyceryl carbonate boiling at 125° to 130° C. at 0.1 to 0.2 mm. can be isolated in substantial yield (*9*).


(4)

Ethylene carbonate reacts with aliphatic and aromatic acids, yielding ethylene glycol esters.


(5)

The light-catalyzed chlorination of ethylene carbonate yields monochloroethylene carbonate and *sym*-dichloroethylene carbonate as products that can be readily isolated (*15*). The former can be dehydrochlorinated by reaction with triethylamine, yielding the expected vinylene carbonate.



Propylene carbonate in general undergoes the same reactions as ethylene carbonate. Propylene carbonate reacts with phenol, yielding the same product, 1-phenoxy-2-propanol, obtained from propylene oxide when an alkaline catalyst is employed (*9*).

Uses of Alkylene Carbonates

In addition to their use in syntheses, the alkylene carbonates have good solvent properties. Ethylene carbonate is an unusually good solvent for polyacrylonitrile, nylon, ethylene terephthalate, and poly(vinyl chloride). A particular application has been in the preparation of solutions of polyacrylonitrile for spinning (*8*). Mixtures of ethylene and propylene carbonate which remain liquid at room temperature have also been used advantageously (*11*). Ethylene carbonate will react with the difficultly soluble terephthalic acid, yielding the ethylene glycol ester, which can then be converted to ethylene terephthalate of high molecular weight (*6*). Ethylene carbonate has been proposed as a solvent for the selective extraction of aromatic hydrocarbons from mixtures with nonaromatic hydrocarbons (*7*).

Because of the ability of ethylene carbonate to react with many substances with the simultaneous evolution of carbon dioxide, it has been proposed as a blowing agent for plastic or elastomeric compositions (*19*).

Ethylene carbonate has been used as a stabilizer in synthetic lubricating oils of the ester type, where it functions by combining with residual acidic groups (*20*).

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