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**PROPYLENE CARBONATE:
PURIFICATION AND TESTS
FOR PURITY**

T. FUJINAGA and K. IZUTSU

*Department of Chemistry, Faculty of Science, Kyoto University,
Sakyo-ku, Kyoto, Japan*

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PROPYLENE CARBONATE: PURIFICATION AND TESTS FOR PURITY

T. FUJINAGA and K. IZUTSU

*Department of Chemistry, Faculty of Science, Kyoto University,
Sakyo-ku, Kyoto, Japan*

Propylene carbonate (4-methyldioxolone-2, 4-methyl-1,3-dioxolan-2-one, propanediol-1,2-carbonate, abbreviated PC in this report) is an odourless, colourless, aprotic solvent with a wide liquid range and a relatively high dielectric constant.

PHYSICAL PROPERTIES OF PC

Some physical properties of PC are summarized in *Table 1*.

Table 1. Physical properties of PC

Freezing point	-49.2°C ^{1*}
Boiling point, 760 mm	241.7°C ¹
Refractive index, n_D^{20}	1.4209 ^{1†}
Density, 25°C	1.198 g/ml ^{2†}
40°C	1.183 g/ml ²
Viscosity, 25°C	2.530 cP ²
40°C	1.916 cP ²
Dielectric constant, 25°C	64.4 ^{2†}
Specific conductance	$1-2 \times 10^{-8}$ ohm ⁻¹ cm ^{-1,3}

* PC is supercooled easily, and it can remain liquid at temperatures as low as -80°C for a period of several months¹.

† For further details of refractive index, density and dielectric constant of PC, see ref. 4.

From the measurements of equilibrium dielectric permittivity, density and refractive index, PC is considered to behave as a normal polar liquid with strong dipole-dipole interactions, but with little or no specific association present⁴.

PC is not hygroscopic to any great extent, but it gradually takes up moisture if exposed to a humid atmosphere. At 25°C, 8.3 g of water can be

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dissolved in 100 g of PC, and the solubility of water increases with temperature. PC is miscible in all proportions with a majority of the common solvents and it readily dissolves many organic compounds and some inorganic salts^{1,2}. It has a dielectric constant, so that dissolved ionic compounds will be extensively dissociated.

PC is a solvent of medium donor properties, similar to those of acetonitrile. Therefore, some similarities are found in the solvations of PC and acetonitrile to cations. The differences in the properties of coordination compounds in these two solvents have been considered to be mainly due to the fact that the PC molecule is large and bulky⁵.

The autoprotolysis constant of PC has not been determined; however, its strength as an acid or a base seems to be moderately weak. Electrochemical studies⁶ show that perchloric acid is completely dissociated in PC but hydrochloric acid is a weak acid. The pK values of dissociations of picric and salicylic acids are 8.0 and 14.1⁶ respectively, which are somewhat smaller than 11.0 and 16.7⁷ respectively in acetonitrile but are much larger than ~ -1.0 and 6.8⁸, respectively, in dimethylsulphoxide and 1.2⁹ and 8.9¹⁰, respectively, in dimethylformamide. The phenomena of homoconjugations between acids and their conjugate anions are also observed in PC⁶, but to a lesser extent than in acetonitrile. Ion conductances in PC are relatively small because of its high viscosity^{3,11}.

Under ordinary conditions of storage, PC is stable¹. Above 200°C, however, appreciable decomposition occurs^{12,16} and traces of acids or bases will promote degradation to propylene oxide, propionaldehyde, allyl alcohol and carbon dioxide¹. PC is hydrolysed fairly rapidly in the presence of acids or bases even at room temperature.

PC is fairly stable to oxidation and reduction. In PC-0.1M tetraethylammonium perchlorate solution, the useful potential range extends from +1.7 to -1.9 V versus aq. SCE on a platinum electrode and from +0.5 to -2.5 V versus aq. SCE on a mercury electrode¹³. PC is relatively stable to attack by halogens anodically liberated at a platinum electrode¹. Moreover, unstable organic radical ions and alkali metals can be stable in pure PC just as in acetonitrile^{13,14}.

PC is essentially non-toxic, either for large single oral doses, by skin absorption, or even on repeated feeding to test animals. While PC is moderately irritating to the mucous membranes of the eyes and respiratory tract, it presents no serious hazards to health in its handling¹.

With these convenient properties, PC has been employed widely as a solvent for various synthetic polymers and as a reaction medium¹. In recent years, it has been receiving increasing attention as an electrochemical solvent². Its principal use appears to be in the development of aprotic electrolytes for high energy batteries¹⁴. It is also promising as a solvent for e.s.r. studies of free radical species¹³, and as an extracting solvent in analytical chemistry¹⁵.

TEST OF PURITY

The major impurities commonly found in PC are water, carbon dioxide, propylene glycol, allyl alcohol, propylene oxide and other unidentified

substances. A gas chromatographic method using a column of Poropak Q has been developed by Jasinski and Kirkland for the analyses of water and these volatile organic impurities¹⁶. Kolthoff, Fujinaga and Izutsu⁶ detected, by conductometric titration with a weak acid, a small amount of uncharged basic substance which is sometimes relatively difficult to eliminate by distillation*.

The following tests can be employed to detect impurities in PC:

(1) Water content by Karl Fischer titration.

(2) Gas chromatographic measurements¹⁶.

This method is most useful. The analytical conditions recommended by Jasinski and Kirkland are shown in *Table 2*. At a column temperature of 70°C, carbon dioxide and water can be detected by using thermal conductivity cells. Propylene oxide, allyl alcohol and some other impurities are detected with a column temperature of 110°C, and 1,2- and 1,3-propylene glycols with a column at 140°C. A flame ionization detector is used for these purposes. The components are identified by matching the retention times with those of pure materials. Determinations can be carried out using standards made by the additions of the pure components to the purified PC. For a 40 μ l-sample, the limits of detections are 1.5 p.p.m. for water, 0.05 p.p.m. for propylene oxide and 0.5 p.p.m. for propylene glycol.

(3) Polarographic measurements.

When tetraethylammonium perchlorate is used as the supporting electrolyte, a deaerated solution prepared from pure PC has a polarographic range extending from +0.5 to -2.5 V versus aq. SCE at a mercury electrode and from +1.7 to -1.9 V versus aq. SCE at a platinum electrode¹³. Propylene glycol impurity will show an anodic wave at a platinum electrode polarized to positive directions. The uncharged, basic impurity which is detectable by the conductometric titration with a weak acid, on the other hand, can give a wave at around -2.0 V versus aq. SCE at a mercury electrode⁶. Water cannot be detected at a mercury electrode, but, in chronopotentiometry or cyclic voltammetry at a platinum electrode in LiClO₄-PC solutions, water from 20 to 500 p.p.m. has been reported to give cathodic and anodic waves between +2.0 and +1.3 V versus Li/Li⁺(1M) electrode^{14, 17}.

(4) Specific conductance measurements.

It is relatively easy to prepare PC that has a specific conductance of $1-5 \times 10^{-8}$ ohm⁻¹ cm⁻¹, but this method is only useful in the detection of ionic impurities. Conductometric titrations of PC with a solution of *p*-toluenesulphonic acid (a weak acid in PC) is sometimes effective for the detection and determination of uncharged, basic impurities as described above⁶.

(5) Spectrophotometric measurements.

Pure PC shows little or no absorption in the u.v. region between 240 and 340 nm, but impure PC does. Therefore, the measurement of an u.v. spectrum in this region seems to be a convenient test of the purity of PC, though the impurities that give the absorption have not yet been identified.

Water at and above the 20 p.p.m. level in PC and in its solutions with LiClO₄ can be determined by differential spectrophotometry employing the 1.9 μ m near infra-red absorption band¹⁸.

* This impurity can be eliminated easily by distillation after the addition of about twice the equivalent amount of an acid (e.g. *p*-toluenesulphonic acid).

Table 2. Conditions for analysis of propylene carbonate¹⁶

Column	2 ft Poropak Q, presieved (80–100 mesh)
Carrier gas—thermal conductivity cell	Dry helium, 100 ml/min
Detector temperature	200°C
Filament current	200 mA
Carrier gas—flame ionization detector	Argon + 1% H ₂ 180 ml/min
Sample size	9 to 40 μ l
Column temperature	70°C for analysis of H ₂ O 110°C for analysis of low boiling organics 140°C for analysis of high boiling organics
Injector temperature	Variable (below 140°C)

PURIFICATION OF PC

PC can be purified fairly easily by fractional distillation under reduced pressure. But, because the presence of trace impurities shows marked effects on the performance of this solvent for high energy batteries, detailed studies have been carried out for the preparation of highly pure solvent. Of these, the study of Jasinski and Kirkland¹⁶ seems to be most thorough. Their purification method is as follows.

Before distillation, 3500 ml of the commercial PC (practical grade 120–22°C/17 mm Hg from Matheson, Coleman and Bell) is percolated at a rate of 10 ml/min down a column of 220 g of dried molecular sieves (Linde 5A, dried by heating at 350°C for 14 hours under a stream of dry argon). By this procedure, the water impurity is reduced to below the limit of detection (<2 p.p.m.).

Distillation is carried out with a Podbielniak Semi-Cal (Series 3650) adiabatic vacuum fractional distillation column. The 'tilting funnel' system is used to control the reflux ratio; the 2 × 72 in. column is filled with Heli-pak (Nichrome). The total charge of PC in the distillation kettle is 3500 ml. A vacuum of 0.5 to 1 mm Hg is achieved at the kettle and its temperature is maintained at 110° to 111°C. The column head temperature levels off between 72° and 75° after the first 100 ml of distillate is collected. A boil-up rate of 200 ml/h is used and the reflux ratio is held between 10:1 and 20:1. The drip spout is placed in the receiver arm to prevent contact of the distillate and the joint. Grease is avoided; Teflon sleeves with Hypalon O-ring are used at the joint; Teflon stopcocks are used to isolate sections of the receiver arm. Distillates are collected and immediately transferred to the inert atmosphere glove box. Table 3 shows the results of gas chromatographic tests for impurities in each section of the distillates.

For further purification, the final 1500 ml of the distillation run described in Table 3 are combined and the low boiling materials are evaporated by passing dry nitrogen gas through the solvent for five days. By this evaporation procedure, low boiling organics are reduced to below 0.4 p.p.m. and water becomes undetectable (below 1.5 p.p.m.); the glycol concentration, however, does not change. The solvent is then redistilled; small amounts of low boiling components (0.7 p.p.m. in total) are detectable only in the first fractions of the distillate and the content of glycol levels off at approximately 11 p.p.m.

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In many electrochemical investigations, procedures which are some modifications or simplifications of the above are employed for the purification of PC^{2, 3, 4, 13, 19-24}. The following procedure can be recommended for general purposes.

Commercial PC is first dried by keeping it overnight with molecular sieves or by passing it through a column of dried sieves (Linde 4A or 5A). Then the PC is subjected to fractional distillation twice under vacuum (one to several mmHg): the middle $\frac{2}{3}$ -fraction of the distillate is collected in each distillation and immediately transferred to an inert atmosphere dry box. The use of an adiabatic vacuum distillation column is highly desirable. By this procedure, the contents of water and organic impurities can generally be reduced to below 20 p.p.m.

Activated alumina²⁰ or dried calcium oxide^{3, 16} have been used as drying materials before distillation. Distillation from calcium oxide has been reported to reduce the content of glycols to about 20 p.p.m. but to increase the content of propylene oxide above its level in the starting material itself¹⁶.

PC after distillation is often stored over molecular sieves (usually Linde 4A) under an inert gas atmosphere. This treatment is useful for removing traces of water and impurities which react with silver ion^{2,3}, but small amounts of ionic substances may be introduced, as detected by the measurement of specific conductance.

Table 3. Distillation run¹⁶

Cumulative volume, ml	Concentrations, p.p.m.			
	H ₂ O	Propylene oxide	Allyl alcohol	Propylene glycol
Starting material	450	33	10	2000
72	35	400	—	—
302	<2	24	—	820
406	<2	6	—	220
856	12	12	2	95
959	9	9	—	—
1159	<2	10	2	58
1266	<2	5	—	49
1466	<2	9	—	27
1601	<2	9	2	15
1801	9	9	3	17
1966	9	6	1	9
2156	4	8	—	12

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