

PHYSICAL CONSTANTS OF SOME ALKYL CARBONATES

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Introduction.

Some of the lower members of the alkyl carbonate series have been prepared as long ago as 80 years, and their boiling points, specific gravities and refractive indices have not been corrected since. These constants were determined sometimes by very poor methods and at different temperatures, and there still exist in the literature fairly wide differences in the above mentioned data. The present research attempts to check the values of some physical constants of seven alkyl carbonates, thus giving the corrected data for them.

The constants determined are: (i) boiling points, (ii) specific gravities, (iii) refractive indices and (iv) molecular refractivities at 15°, 20°, and 50° C.

Apparatus and methods used.

Specific gravities were determined by Sprengel-Ostwald's U-shaped pycnometer¹⁾ of about 9 cc. capacity, but for di-*iso*-propyl and di-*n*-propyl carbonates a small 2 cc. pycnometer of the same type was used.

The observed specific gravities were reduced to vacuum by applying the formula: $d_4^{t^0} = F \cdot \frac{Q - 0,0012}{w} + 0,0012$ (where F = weight of substance, w = weight of water, Q = density of water at t^{02}).

Both pycnometers were also checked, a difference being found in the fourth decimal place only.

Refractive indices were determined by an Abbé's refractometer, supplied by Goertz & Co., Germany. For the calculation of molecular refractivities the Lorenz-Lorenz formula was applied³⁾.

1) Fr. Kohlrausch, Lehrbuch der praktischen Physik, 1921, p. 63.

2) W. A. Roth und F. Eisenlohr, Refraktometrisches Hilfsbuch, 1911, p. 68.

3) W. Nernst, Theoretische Chemie, 1921, p. 359.

$$M_r = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

The temperatures were recorded to an accuracy of 0,1° C. A corrected (normal) thermometer was always used. The determinations of boiling points were made with a set of thermometers, 50° C interval each (i.e., 0°—50°, 50°—100°, 100°—150°, etc.), tested at the Physikalisch-Technische Reichsanstalt at Charlottenburg, Germany (certificate dated 10. June 1925).

As it was difficult to keep the temperature constant at 50° C for a long time, the refractive indices were recorded at the moment, when the liquid very slowly reached the desired temperature, and on cooling passed this point again; the difference between the two observations did not exceed 0,0002 units.

Experimental.

1. Dimethyl carbonate, $\text{OC}(\text{OCH}_3)_2$, mol. wt. 90.046.

A pure preparation, supplied by C. A. F. Kahlbaum Ltd., Berlin, three times refractionated, was used. The figures below are an average of two determinations.

a) B. P.: 90'5° C (corr.). Recorded: 90.6° (corr.) [C. Councler¹) and B. Röse²)], 91°/732 mm.Hg. [L. Schreiner³)] and 89.7° adopted for International Critical Tables⁴).

b) Specific gravities:

$$d_4^{150} = 1,0759; \quad d_4^{200} = 1,0694; \quad d_4^{500} = 1,0295.$$

Recorded: $d^{220} = 1,069$ [Councler¹)]; $d^{170R} = 1,065$ [B. Röse²)];

adopted for I. C. T.: $d^{220} = 1,069$.

c) Refractive indices. Table I, given below, shows the results of determinations of refractive indices and molecular refractivities.

Given by B. Röse²): $n^{22-230} = 1,3748$; calculated on the

base of Table I: $n^{22.50} = 1,3769$, diff.: = 0,0021 units.

1) C. Councler, Ber. 13, 1698 (1880).

2) B. Röse, Annalen 205, 232 (1880).

3) L. Schreiner, J. pr. Chem. (2) 22, 357 (1880).

4) International Critical Tables, by the National Research Council of U. S. A., Vol. 1, 1926.

Table I.

Refractive indices of dimethyl carbonate.

Temp. °C	n _D	lg $\frac{n^2-1}{n^2+2}$	Mol. refr. : R _L ¹⁾		Difference per cent
			Observed	Calculated	
15°	1,3725	$\bar{1},35708$	19,04	.	—0,35
20°	1,3687	$\bar{1},35310$	18,94	19,35	—0,45
50°	1,3463	$\bar{1},32869$	18,64		—0,79

2. Diethyl carbonate, OC(OC₂H₅)₂; mol. wt. 118.08. Diethyl carbonate is the most widely investigated alkyl carbonate. It has been synthesised from diethyl oxalate by the action of sodium (or potassium) by Löwig & Weidemann²⁾, and Schreiner³⁾; from ethyl iodide and silver carbonate by Clermont⁴⁾ and Kopp⁵⁾; from ethyl alcohol and ethyl chlorocarbonate by Brühl⁶⁾; by adding ethyl chloroformate and absolute alcohol to powdered potassium cyanide in absolute alcohol, by Druschel and Knapp⁷⁾; from phosgene and ethyl alcohol in presence of dialkyl-aniline by Boehringer and Soehne⁸⁾. Further it was obtained as a byproduct by Wurz⁹⁾, Chancel¹⁰⁾, Ladenburg and Wichelhaus¹¹⁾.

The present authors used: (i) a purified C. A. F. Kahlbaum's preparation, and (ii) a preparation, synthesised by the Löwig & Weidemann's method. The preparations were identical.

a) B. P.: 125.8° (corr.). Recorded: 127—129° [Curtis¹²⁾]; 125.8° (corr.) [Kopp⁶⁾]; 126.7—127.2° (corr.) [Perkin¹³⁾]; 126.8°/760 mm.

1) Adopted from the International Physico-chemical Symbols, publ. by the Chemical Society, see J. Chem. Soc. April 1921, p. 505.

2) Löwig & Weidemann, *Annalen* 36, 301 (1840).

3) loc. cit.

4) Ph. v. Clermont, *Annalen* 91, 376 (1854).

5) H. Kopp, *ibid.* 95, 325 (1855).

6) J. W. Brühl, *ibid.* 203, 23 (1880).

7) W. Druschel und D. Knapp, *Chem. Zentr.* 1916, I, 144.

8) C. Boehringer u. Soehne, *ibid.* 1922, IV, 44.

9) A. Wurz, *Annalen* 79, 286 (1851).

10) G. Chancel, *Jahresber.* 1851, 512.

11) A. Ladenburg u. Wichelhaus, *Annalen* 152, 165.

12) Curtis, *Am. Chem. Journ.* 19, 698 (1836).

13) Perkin, *Journ. Chem. Soc.* 65, 421.

Hg. [Luginin¹⁾]; 126—126.4°/748 mm.Hg. [Brühl²⁾]; in I. C. T. 125.8°.

b) Sp. gravity: $d_4^{150} = 0.9808$; $d_4^{200} = 0.9752$; $d_4^{500} = 0.9415$.

Recorded: $d_4^{200} = 0.9762$ [Brühl²⁾] and $d_4^{20} = 0.979$ [K. v. Auvers]; the latter is adopted for I. C. T.

c) Refractive index and mol. refractivity of diethyl carbonate are given in Table II below:

Table II.
Refractive indices of diethyl carbonate.

Temp. °C	n_D	$\lg \frac{n^2-1}{n^2+2}$	R_L		Difference per cent
			Observed	Calculated	
15°	1,3887	$\bar{1},37355$	28,47		-0,10
20°	1,3852	$\bar{1},37006$	28,39	28,58	-0,15
50°	1,3635	$\bar{1},34756$	27,92		-0,56

Recorded: $n_D^{200} = 1,38523$ [Brühl²⁾]; $n_{He}^{14,750} = 1,38780$ [K. v.

Auvers³⁾]; in I. C. T. 1.3852, which corresponds to our figure.

III. Di-*n*-propyl carbonate, $OC(OC_3H_7)_2$, mol. wt. 146.11. Di-*n*-propyl carbonate has been prepared by two methods: Röse⁴⁾ synthesised it from sodium propylate and *n*-propyl chlorocarbonate, while Cahours⁵⁾ obtained it by the action of sodium on dipropyl oxalate.

In the present research the ester was prepared by Röse's method, slightly modified, taking pure propyl alcohol (in excess) instead of sodium propylate.

(50 gm. of propyl chlorocarbonate and 26 gm. of propyl alcohol yielded 40 gm. of pure di-*n*-propyl carbonate.)

a) B. P. of di-*n*-propyl carbonate was 168.5° (corr.). Recorded: 168.2° (corr.) [Röse⁴⁾], also in I. C. T.].

1) Luginin, Bull. Soc. chim. (3) 15, 47.

2) loc. cit.

3) K. v. Auvers, Chem. Zentr. 1923, III, 544.

4) loc. cit.

5) A. Cahours, Jahresber. 1874, 333 (1876).

b) Sp. gravity: $d_4^{150} = 0,9460$; $d_4^{200} = 0,9411$; $d_4^{500} = 0.9107$.

The figures recorded show fairly wide differences, namely: $d^{170} = 0,949$ [B. Röse]; $d^{220} = 0.968$ [Cahours], adopted for I. C. T. The difference = 0.021 units.

c) Refractive indices and molecular refractivities are given in Table III below: —

Table III.
Refractive indices of di-*n*-propyl carbonate.

Temp. °C	n_D	$\lg \frac{n^2-1}{n^2+2}$	R_L		Difference per cent
			Observed	Calculated	
150	1,4048	$\bar{1},38915$	37,84		+0,01
200	1.4014	$\bar{1},38592$	37,75	37,82	-0.04
500	1,3799	$\bar{1},36471$	37,16		-0,45

Recorded: $n^{22} - 230} = 1.3980$ [B. Röse]. Interpolated from Table III, $n_D^{22.5} = 1,3997$; diff. = + 0,0017.

IV. Di-*iso*-propyl carbonate, $OC[OCH(CH_3)_2]_2$, mol. wt. 146,11. The authors did not find any description of this ester in the literature and it is left out in the C-table of I. C. T.

Procedure. — The ester was prepared by boiling (on an oil-bath) *iso*-propyl iodide with silver carbonate. After the products of reaction were separated by distillation, the distillate was boiled once more with silver carbonate. The fraction b. p. 146—147°C was taken for analysis. A test for presence of iodide gave negative results. This fraction was redistilled until constant boiling point and refractive index were obtained.

a) B. P. of di-*iso*-propyl carbonate: 147.2° (corr.).

b) Sp. gravity: $d_4^{150} = 0.9212$; $d_4^{200} = 0.9162$; $d_4^{500} = 0.8846$.

c) The following Table IV shows the determinations of refractive index and molecular refractivity: —

Comparing these data with those of the normal ester, we can conclude that the general rule¹⁾ is applicable to this case

1) J. B. Cohen, Organic chemistry for advanced students, II, 22 (1919).

Table IV.
Refractive indices of di-*iso*-propyl carbonate.

Temp. °C	n_D	$\lg \frac{n^2-1}{n^2+2}$	R_L		Difference per cent
			Observed	Calculated	
15°	1,3967	$\bar{1},38139$	38,17		+0,24
20°	1,3932	$\bar{1},37799$	38,08	37,82	+0,17
50°	1,3715	$\bar{1},35604$	37,50		-0,22

too, *i. e.*: the molecular refractivity of di-*iso*-propyl carbonate is identical with that of the normal ester, but the boiling point and specific gravity are lower.

V. Di-*n*-butyl carbonate, $OC(OC_4H_9)_2$, mol. wt. 174.14. This ester has been prepared previously by Lieben and Rossi¹⁾ from silver carbonate and *n*-butyl iodide.

The present authors synthesised it from *n*-butyl chlorocarbonate and *n*-butyl alcohol by boiling on an oil-bath. The reaction proceeded very smoothly. [44 gm. of *n*-butyl chlorocarbonate and 30 gm. of *n*-butyl alcohol yielded 40 gm. of pure ester].

a) B. P.: 207.5° (corr.). Recorded: 207° (corr.)/740 mm. [Lieben and Rossi]; in I. C. T. (p. 230): 207,7° C.

b) Specific gravity: $d_4^{150} = 0.9283$; $d_4^{200} = 0.9238$; $d_4^{500} = 0.8961$.

Recorded: $d^{00} = 0.9407$; $d^{200} = 0.9244$; $d^{400} = 0.9111$ [Lieben and Rossi]. Adopted in I. C. T.: 0.924 (20°). All these figures are very close to ours.

c. Molecular refractivities are given in Table V below: —

Table V.
Refractivities of di-*n*-butyl carbonate.

Temp. °C	n_D	$\lg \frac{n^2-1}{n^2+2}$	R_L		Difference per cent
			Observed	Calculated	
15°	1,4152	$\bar{1},39885$	46,97		-0,05
20°	1,4117	$\bar{1},39562$	46,85	47,06	-0,12
50°	1,3917	$\bar{1},37646$	46,21		-0,50

1) A. D. Lieben und A. Rossi, Annalen 165, 112 (1874).

VI. Di-*iso*-butyl carbonate $\text{OC}[\text{OCH}_2\text{CH}(\text{CH}_3)_2]_2$, mol. wt. 174. 14.

For the preparation of di-*iso*-butyl carbonate, A. Wurz¹⁾ heated silver carbonate and *iso*-butyl iodide in sealed tubes, while B. Röse²⁾ used for the same purpose *iso*-butyl chlorocarbonate and *iso*-butyl alcohol.

The latter procedure was applied also by the present authors: a mixture of *iso*-butyl carbonate (44 gm.) and *iso*-butyl alcohol (30 gm.) was boiled on an oil-bath for 4—5 hrs., in the beginning a considerable amount of HCl was eliminated, the reaction proceeded quietly; yield: 40 gm. of pure ester, or 70 per cent of theory.

a) B. P.: 189.8° (corr.). Recorded: 190° [A. Wurz]; 190.3° [B. Röse, also in I. C. T.].

b) Sp. gravity: $d_4^{15^\circ} = 0.9186$; $d_4^{20^\circ} = 0.9138$; $d_4^{50^\circ} = 0.8849$.

Recorded: $d^{15^\circ} = 0.919$ [B. Röse, in I. C. T.].

c) Refractive indices are given in Table VI below: —

Table VI.
Refractivities of di-*iso*-butyl carbonate.

Temp. °C	n_D	$\lg \frac{n^2-1}{n^2+2}$	R_L		Difference per cent
			Observed	Calculated	
15°	1,4107	$\bar{1},39469$	47,01		—0,03
20°	1,4072	$\bar{1},39141$	46,90	47,06	—0,10
50°	1,3859	$\bar{1},37073$	46,19		—0,50

Recorded: $n^{22-23^\circ} = 1.4048$ [B. Röse]. Interpolated from Table VI: $n^{22.5^\circ} = 1.4055$.

VII. Di-*iso*-amyl carbonate, $\text{OC}[\text{O}(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2]_2$, mol. wt. 202. 17. Di-*iso*-amyl carbonate may be synthesised according to J. Bruce³⁾ by the action of potassium or sodium on

1) A. Wurz, Annalen 93, 119 (1855).

2) loc. cit.

3) J. Bruce, Annalen 85, 16 (1853).

di-*iso*-amyl oxalate; B. Röse¹⁾ prepared it from *iso*-amyl chloroformate and *iso*-amyl alcohol. The method of Bruce was chosen for the present research, but it was found, that excess of sodium should be avoided, otherwise the ester chars (for 20 gm. of *iso*-amyl oxalate only 1 gm. of sodium can be used). The ester formed was found to be identical with the preparation supplied by C. A. F. Kahlbaum & Co.

a) B. P.: 233° (corr.)²⁾. Recorded: 226° [J. Bruce³⁾]; 228.7° [Röse, also in I. C. T.].

b) Sp. gravity: $d_4^{150} = 0.9110$; $d_4^{200} = 0.9067$; $d_4^{500} = 0.8807$.

Recorded: $d^{15.50} = 0.9065$ [Bruce]; $d^{150} = 0.912$ [Röse and I.

C. T.].

c) Table VII shows the results of determinations of refractive index: —

Table VII.

Refractive indices of di-*iso*-amyl carbonate.

Temp. °C	n_D	$\lg \frac{n^2-1}{n^2+2}$	R_L		Difference per cent
			Observed	Calculated	
15 ⁰	1,4208	1,40395	56,26		—0,01
20 ⁰	1,4174	1,40086	56,12	56,29	—0,08
50 ⁰	1,3965	1,38120	55,20		—0,50

Recorded: $n^{22-230} = 1,4153$ [Röse]. Interpolated from Table VII:
 $n^{22.50} = 1,4157$.

Summary. The boiling points, specific gravities and refractivities of six known and one new (di-*iso*-propyl carbonate) alkyl carbonates were determined. As regards the boiling points, very little difference was found between the authors corrected values and those recorded in the literature, except in the case of di-*iso*-

1) loc. cit.

2) When an ordinary thermometer, calibrated from 0° to 360°, is used, the temperature observed is 226°.

3) loc. cit.

amyl carbonate, when the difference amounts to about 6° C. Wider differences are found in specific gravities and refractivities. If the specific gravities and refractivities of each ester are plotted against temperature, they would lie on a straight line.

The difference between the observed molecular refractivity and that calculated from atomic refractivities increases with the temperature, amounting to 0.79% at 50° in the case of dimethyl carbonate.

The coefficient or correction of refractive index per degree is constant for all esters below 20° C, and amounts to 0.00070. But for temperatures between 20°—50° C it is slightly higher, on an average: 0.00072. This value is twice the value given by A. F. Joseph ¹⁾ for fixed oils.

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1) A. F. Joseph, The change of refractive indices of fixed oils with temperature, Journ. Soc. Chem. Indust., Vol. XXXIX, No 5, p. 66 (1920).