On the Reaction between Carbon Monoxide and Alcohol Catalyzed by Alcoholate

II. The Propyl- and Butyl Alcohols

Appendix: The Solubility of Carbon Monoxide in Secondary and Tertiary Butyl Alcohol

J. CHR. GJALDBÆK

*Department of Inorganic Chemistry, Royal Danish School of Pharmacy,
Copenhagen, Denmark*

In an earlier paper [1] the kinetics of the reactions of carbon monoxide with methanol and ethanol solutions of the corresponding alcoholates, giving alkyl formates, were investigated. The present paper deals with the kinetics of the analogous reactions in the two propyl alcohols and the four butyl alcohols.

MATERIALS

Carbon monoxide was prepared by adding anhydrous formic acid to concentrated sulphuric acid. It was passed through soda lime and collected in a glass bulb gasometer over concentrated sulphuric acid. By analysis in a micro-gas-burette [2] the gas was found to contain more than 99 % carbon monoxide, the rest being air.

The alcohols were dried by slow distillation in a wire-gauze column [3]. The boiling points (corrected to 760 mm) were: normal propyl alcohol 97.4°, isopropyl alcohol 82.4°, normal butyl alcohol 117.7°, isobutyl alcohol 107.9°, secondary butyl alcohol 99.5° and tertiary butyl alcohol 82.4° (m. p. 25.6°).

The alcoholates were prepared by dissolving sodium in the alcohols in question except in the case of tertiary butyl alcohol where potassium was used on account of the slight solubility of sodium butylate in tertiary butyl alcohol.

PROCEDURE

The velocities of the reactions were determined in a Brønsted shaking apparatus. For descriptions of the apparatus, the procedure, and the method of treatment of the data see the paper cited [1]. The volume of the reaction flask was 108.4 ml and the dead space from the neck of the flask to the surface of the mercury in the manometer was 17.5 ml; in each experiment 25.00 ml of catalyst solution was introduced.

In the earlier paper all pressure readings were corrected, since it was observed in blank experiments with pure alcohol in both flasks that on addition of carbon monoxide to the reaction flask the pressure did not immediately rise to its final value. Blank experiments were also carried out with the propyl and butyl alcohols, but since the increase of pressure in all cases was less than 0.2 cm (no doubt because of the smaller vapour pressure of these alcohols) corrections were not necessary.

EXPERIMENTAL RESULTS AND DISCUSSION

A survey of the experimental results is given in Tables 1 and 2 where the velocity constants are calculated on the basis of natural logarithms and seconds.

All the reactions were found to be first order with respect to carbon monoxide. At every temperature the experiments were carried out at several con-

Table 1. $CO + C_3H_7OH$; catalyst C_3H_7ONa.

	Temp. °C	$c_{cat.}$	$\dfrac{\text{Mol ester}}{\text{Mol CO}_{abs.}}$	$k \cdot 10^5$ s^{-1}	$\dfrac{k \cdot 10^5}{c_{cat.}}$	$k° \cdot 10^5$ s^{-1}	$k' \cdot 10^5$ s^{-1}
Normal	20.0	0.9846 0.4672	— 1.00	3.089 1.233	3.137 2.639	2.262	53.89
	30.0	1.013 0.5044 0.2632	0.95 0.98 0.98	9.650 3.990 1.965	9.526 7.911 7.466	6.780	157.2
	40.0	0.9870 0.4766 0.2903	1.01 1.01 1.06	28.97 11.20 6.520	29.35 23.51 22.45	19.77	443.0
Iso	20.0	0.2038 0.0989	1.05 0.99	1.589 0.7597	7.798 7.681	7.577	168.7
	40.0	0.2410 0.1492	1.02 1.06	11.63 6.730	48.24 45.11	40.47	836.3

Table 2. $CO + C_4H_9OH$; catalyst C_4H_9ONa, except in the experiments with tertiary C_4H_9OH where tertiary C_4H_9OK was used as catalyst.

	Temp. °C	$c_{\text{cat.}}$	$\dfrac{\text{Mol ester}}{\text{Mol CO}_{\text{abs.}}}$	$k \cdot 10^5$ s^{-1}	$\dfrac{k \cdot 10^5}{c_{\text{cat.}}}$	$k° \cdot 10^5$ s^{-1}	$k' \cdot 10^5$ s^{-1}
Normal	30.0	0.8477	1.02	7.409	8.740		
		0.4847	1.05	3.684	7.601	5.991	149.4
		0.3347	1.03	2.302	6.878		
	40.0	0.4907	—	10.71	21.82		
		0.4579	0.96	9.899	21.62	16.98	411.5
		0.2911	1.07	5.756	19.77		
	50.0	0.4725	1.02	25.98	54.98	40.38	951.9
		0.2418	—	11.97	49.51		
Iso	20.0	0.3180	0.96	1.919	6.033	4.604	111.5
		0.2080	—	1.143	5.495		
	40.0	0.2722	—	12.52	46.00	39.04	884.8
		0.1914	0.95	8.394	43.86		
Secondary	20.0	0.3922	1.02	5.284	13.47		
		0.2934	1.01	3.534	12.04	9.375	237.6
		0.1740	1.05	1.911	10.98		
	40.0	0.5813	—	63.12	108.6		
		0.3485	0.90	30.43	87.31		
		0.2893	—	23.48	81.17	62.23	1473
		0.1539	0.97	11.13	72.30		
Tertiary	26.1	0.7382	1.02	25.94	35.14		
		0.4964	1.05	13.85	27.90	17.78	391.9
		0.2327	1.00	5.142	22.10		
	30.0	1.025	—	64.46	62.89		
		0.5552	—	25.04	45.09	26.82	568.6
		0.2501	—	8.058	32.22		
	40.0	0.5534	1.01	47.20	85.29		
		0.2835	1.09	19.65	69.30	56.38	1098
		0.2344	1.12(?)	15.81	67.44		

centrations of the catalyst and as in the earlier paper the velocity constants were extrapolated to $c_{cat.} = 0$ according to the equation

$$\log \frac{k}{c_{cat.}} = \log k^\circ + \beta \cdot c_{cat.}$$

In quantity k' is given by the equation

$$k' = k^\circ \cdot \left(\frac{V_g}{V_l} + a \right) \frac{1}{a} \text{*} \tag{1}$$

where V_g and V_l are the volume of the gas phase and liquid phase, respectively, and a is the distribution coefficient of carbon monoxide between the liquid and the gas phase (*i. e.* the Ostwald absorption coefficient). The values of the absorption coefficient for carbon monoxide in the propyl alcohols and in normal and isobutyl alcohol have been determined by the author [4]; for secondary and tertiary butyl alcohol see the appendix to this paper.

The values of $k' \cdot 10^5$ for methanol and ethanol are calculated to be

|	35.05°	45.05°	54.16°
Methanol	53.28	136.0	358.3
Ethanol	180.9	475.6	1052

In an experiment with 0.1682 molar sodium butylate in tertiary butyl alcohol at 30° the value $k \cdot 10^5/c_{cat.} = 44.5$ was found; thus with sodium alcoholate the reaction is a little faster than with potassium alcoholate. The same result was obtained in an experiment with 0.6208 molar potassium butylate in secondary butyl alcohol at 40° where $k \cdot 10^5/c_{cat.}$ was found to be 96.7 (*cf.* Table 2).

After each experiment 5.00 ml of the cooled reaction mixture was diluted with 50 ml of carbon dioxide-free water, allowed to stand long enough for complete hydrolysis of the ester, and titrated with 0.1 N hydrochloric acid. As in the earlier paper the ester concentrations so found are approximately equivalent to the amount of carbon monoxide absorbed; the results are given in Tables 1 and 2.

In nearly all the experiments small amounts of a sodium formate sediment appeared. When dissolved in water and neutralized the sediment reduced mercuric chloride to mercurous chloride and on distillation with sulphuric

---

* The corresponding equation though without the a in the parenthesis was used in the earlier paper. Professor Verner Schomaker of the California Institute of Technology, Pasadena, who has been kind enough to correct the translation into English, called attention to this mistake.

acid it evolved formic acid. A 0.672 g sample of the washed and dried sediment after heating neutralized 10.00 ml of 0.1 N hydrochloric acid (theoretical 10.20 ml). Since it was difficult to determine the small amounts of sediment quantitative analysis was carried out in only a few cases. It can be estimated that the amount of sediment in all experiments was less than about 5 % of the amount of sodium alcoholate. The formation of sodium formate can be explained according to the equation

$$HCOOR + RONa = R_2O + HCOONa$$
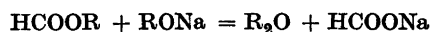
where R denotes the alcohol radical. This equation implies that the concentration of the catalyst decreases as the reaction proceeds. In most of the experiments the time of earliest appearance of sediment was noted; however, in no case did the formation of the sodium formate appear to influence the velocity constant, undoubtedly because the alteration in concentration of the catalyst was only slight.

In many of the experiments the reaction proceeded to an equilibrium considerably short of complete absorption of the carbon monoxide. Since the concentration of the ester was determined and the concentration of carbon monoxide is known from the final pressure the equilibrium constant of the gross reaction $CO + ROH = HCOOR$ can be calculated; however, in many of the experiments the final pressure of carbon monoxide was too small to give more than a crude estimate. At 40° the equilibrium constant for ester-formation in tertiary butyl alcohol may be estimated to be about 4 l/M, in normal and secondary butyl alcohol about 6, in isobutyl alcohol about 8 and in propyl alcohol about 11.

Table 3.

Alcohol	Methyl	Ethyl	Normal propyl	Iso-propyl	Normal butyl	Iso-butyl	Sec. butyl	Tert. butyl
A	4357	4037	4198	3191	3941	4129	3637	2960
H	10.85	10.36	11.05	8.12	10.19	11.14	9.78	7.50
Solubility * 20°	> 1	> 1	> 1	0.22	> 1	0.63	0.66	0.34 27°

* Approximate molarity of saturated solution of sodium alcoholate in the corresponding alcohol.
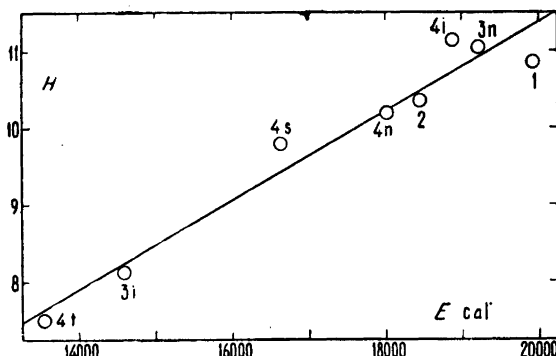
Fig. 1. *1:* CH_3OH; *2:* C_2H_5OH; *3n:* $n\text{-}C_3H_7OH$; *3i:* $iso\text{-}C_3H_7OH$; *4n:* $n\text{-}C_4H_9OH$; *4i:* $iso\text{-}C_4H_9OH$; *4s:* $sec.\text{-}C_4H_9OH$; *4t:* $tert.\text{-}C_4H_9OH$.

The quantities A and H of the equation

$$\log k' = -\frac{A}{T} + H$$

were calculated by the method of least squares. The results are recorded in Table 3 together with values for the earlier methyl and ethyl alcohol data [1] recalculated according to the new solubility measurements [4] and to the corrected equation (1). The values of A and H for isopropyl and isobutyl alcohol are the least exact since these values are based on only four experiments in each alcohol. In Fig. 1 the frequency exponent H is plotted as ordinate and the energy of activation E ($E = 4.571\ A$) as abscissa, the straight line representing the equation

$$H = \frac{E}{1720} - 0.24$$

obtained by least squares on the assumption of linear dependence.

Calculation of the number of collisions S from the formula

$$S = \sigma_{1,2}^2\, n_1 n_2 \sqrt{8\pi RT \frac{M_1 + M_2}{M_1 M_2}}$$

where $\sigma_{1,2}$ denotes the sum of the collision radii of the molecules, n the number of molecules per ml, and the M's the molecular weights, leads to values of $\log S$ at unit concentrations (1 M/l) between 11.1 and 11.4 for all the alcohols,

Table 4. Values of densities and vapour pressures of the alcohols used in the calculations.

Temp.	Secondary butyl alcohol		Tertiary butyl alcohol	
	$d \dfrac{t^5}{4}$	Vapour pressure mm Hg [6]	$d \dfrac{t}{4}$	Vapour pressure mm Hg [9]
20.0	0.8073	16.2		
26.0			0.7804 [7]	44.3
30.0	0.8000	27.7	0.7762 [7]	56.9
40.0	0.7922	45.9	0.7630 [8]	102.3
50.0	0.7834	74.0	0.7522 [8]	174.3

S being expressed in M/l per s. Since the literature, as far as the author is aware, does not contain data for the radii of the propyl and butyl alcohols, the radii were estimated with the help of Fisher-Hirschfelder-Taylor atom models of the alcohols on the basis of the value 2 Å known for methanol from its viscosity; the estimates all lie between 2 and 3.5 Å. The further values $\sigma_{CO} = 1.6$ Å and $T = 318$ were used. Only for isopropyl alcohol, secondary butyl alcohol and tertiary butyl alcohol are the values of H markedly different from the calculated log S.

Saturated solutions of the alcoholates were titrated with 0.1 N hydrochloric acid; the approximate molarities are recorded in Table 3.

APPENDIX: THE SOLUBILITY OF CARBON MONOXIDE IN SECONDARY AND TERTIARY BUTYL ALCOHOL

By a procedure and in an apparatus earlier described [4] the solubilities of carbon monoxide in secondary and tertiary butyl alcohol were determined at different temperatures. The boiling points of the alcohols used are recorded on p. 683 of this paper. For values of densities and vapour pressures used in the calculations see Table 4. The solubilities expressed by means of Ostwald's absorption coefficient are recorded in Table 5. Smoothed values at different temperatures are recorded in Table 6, where also u and log a according to the equation

$$\log l = \frac{u}{RT} + \log a$$

are given. The extraordinary high temperature coefficient for the solubility in tertiary butyl alcohol should be noticed.

5

*Table 5. Solubility of carbon monoxide in the butyl alcohols.*

Secondary			Tertiary		
t	l	l	t	l	l
20.05	0.168		27.56	0.194	
20.10		0.164	27.75		0.195
35.40	0.173		35.57	0.206	
35.50		0.170	35.60		0.208
49.98	0.180		49.98	0.226	
50.25		0.176	50.28		0.227

Table 6. Smoothed values of the solubility of carbon monoxide in the butyl alcohols.

Temp.	20°	26°	30°	40°	50°	dl/dt	u	$\log a$
Secondary	0.166		0.170	0.174	0.178	0.00040	— 438	— 0.45
Tertiary	·	0.192	0.198	0.213	0.226	0.00142	— 1320	+ 0.24

SUMMARY

1. The reactions between carbon monoxide and six alcohols (the two propyl and the four butyl alcohols), catalyzed by the corresponding alcoholates, are investigated manometrically. Esters of formic acid and the alcohol in question are formed. The rate is found to be of the first order with respect to carbon monoxide. The rate is shown to be determined by the reaction

$$CO + RO^- = (COOR)^-$$
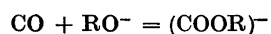
the complex formed reacting to give HCOOR and RO⁻ which thus acts as a catalyst, R denoting the alcohol radical.

2. The velocity constant increases somewhat faster than proportional to the concentration of the catalyst and is approximately described by the equation

$$\log \frac{k}{c_{\text{cat.}}} = k° + \beta \cdot c_{\text{cat.}}$$

3. All the experiments are carried out at two or three temperatures and a survey of the results is given in Tables 1 and 2. Using the method of least squares A and H are calculated according to the equation

$$\log k' = -\frac{A}{T} + H$$

where $4.571 \cdot A$ is the energy of activation (E) and H the frequency exponent. The results are together with recalculated values for the reaction in methanol and ethanol recorded in Table 3. Linear dependence between E and H is shown in Fig. 1.

4. In most of the experiments small amounts of sodium formate sediment appeared (less than 5 % of the amount of sodium alcoholate). The formation can be explained according to the equation

$$HCOOR + RONa = R_2O + HCOONa$$
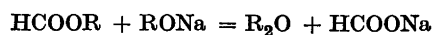
involving a decrease of the concentration of the catalyst which, however, did not alter the velocity constant notably.

5. In many of the experiments the reaction proceeded to an equilibrium. The equilibrium constant

$$K = \frac{c_{ester}}{c_{CO} \cdot c_{alcohol}}$$

was in tertiary butyl alcohol roughly estimated to be about 4, in normal and secondary butyl alcohol about 6, in isobutyl alcohol about 8 and in normal propyl alcohol about 11 at 40°.

6. Approximate solubilities of the sodium alcoholates, determined at 20°, are recorded in Table 3.

7. Appendix. The solubility of carbon monoxide in secondary and tertiary butyl alcohol is determined at different temperatures ranging from 20° to 50°. Smoothed values of the solubilities are recorded in Table 6.

REFERENCES

1. Christiansen, J. A., and Gjaldbæk, J. Chr. *Kgl. Danske Videnskab. Selskab Mat.fys. Medd.* **XX** (1942) no. 3.
2. Christiansen, J. A., and Wulff, I. *Kgl. Danske Videnskab. Selskab Mat.fys. Medd.* **XXII** (1945) no. 4.
3. Klit, A. *Fraktioneret Destillation* København (1943).
4. Gjaldbæk, J. Chr. *Kgl. Danske Videnskab. Selskab Mat. fys. Medd.* **XXIV** (1948) no. 13.
5. Pickard, R. H., and Kenyon, J. *J. Chem. Soc.* **99** (1911) 45.
6. Gilliland, E. R., and Sherwood, T. K. *Ind. Eng. Chem.* **26** (1934) 519.
7. Timmermans, J., et Delcourt, Y. *J. chim. phys.* **31** (1934) 85.
8. Paterno, E., e Mieli, A. *Atti reale accad. Lincei* (5) **16** (1907) 153.
9. Parks, G. S., and Barton, B. *J. Am. Chem. Soc.* **50** (1928) 25.