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ON THE REACTION BETWEEN  
CARBON MONOXIDE AND ALCOHOL  
CATALYZED BY ALCOHOLATE

BY

J. A. CHRISTIANSEN AND J. C. GJALDBÆK



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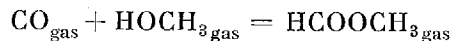
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### Introduction.

In 1914, A. STÄHLER (1) showed that CO combines with dry R<sub>2</sub>ONa (R = alcy) to form NaCOOR or C(OR)(ONa), but not RCOONa in detectable amounts. Moreover, he found that at a pressure of a few hundred atmospheres and at a temperature of 100—200°, CO also combines with alcoholates dissolved in the corresponding alcohol, forming alcyformates, the alcoholate acting as a catalyst.

The experiments were merely preparative, and no exact investigation of the kinetics of the reaction was intended. The author states, however, that the reaction was faster with methanol than with ethanol. Our experiments prove that, at pressures below 1 atm. and correspondingly lower temperatures, the reaction still proceeds at a measurable rate, but about 3 times faster in the case of ethanol than in the case of methanol.

In 1926, it was shown by one of the present authors (2) that the equilibrium



can be attained using solid NaOCH<sub>3</sub> as a catalyst, and that the equilibrium constant K<sub>c</sub> is approximately given by the expression

$$\log K_c = 1880/T + 4.82.$$

The present paper deals with the kinetics of the reaction which so far has not been investigated, except by STÄHLER.

### Materials.

CO was prepared according to L. MOSER (3). Anhydrous formic acid was added drop by drop to concentrated sulphuric acid in a small flask; the CO evolved was led through soda

lime to free it from  $\text{CO}_2$  and was collected in a glass bulb gasometer of the BODENSTEIN type over concentrated sulphuric acid. By analyses in a micro-gas-burette (4), the gas was found to contain about 98%  $\text{CO}$ —the balance being air and, strangely enough, traces (about 0.5%) of  $\text{CO}_2$ . These small impurities were considered harmless and no further purification was attempted.

Anhydrous alcohols were prepared according to HAKON LUND and J. BJERRUM (5), omitting, however, the distillation from tribromobenzoic acid. The preparations were tested as follows.

Methanol:

a) 10 ml. did not decolorize 1 drop of 0.1 n  $\text{KMnO}_4$  in the course of 15 min. (no aldehyde).

b) 10 ml. consumed less than 1 drop of 0.1 n  $\text{NaOH}$  (no formate) and less than 1 drop of 0.1 n  $\text{HCl}$  (no base).

c) 5 ml. + 10 ml. of 2 n  $\text{NaOH}$  + 25 ml of 0.1 n  $\text{I}_2$  remained clear after standing for 5 minutes and gave no odour of iodoform (no acetone).

Ethanol:

10 ml. did not decolorize 5 drops of 0.1 n  $\text{KMnO}_4$  in the course of 30 min. (no aldehyde).

No acid or basic impurities as under methanol.

Preparation of sodium alcoholate. Freshly cut sodium was freed from kerosene by means of filter paper and dissolved in anhydrous alcohol. It was stored in portions of 100 to 200 ml. in cork-stoppered flasks and was protected against  $\text{CO}_2$  by means of soda lime. After dilution with water the solutions were titrated with 0.1 n  $\text{HCl}$  and methyl red as indicator. The concentrations at higher temperatures were calculated by means of the following table which is based on YOUNG'S (6) measurements for pure alcohols.

Table of Specific Gravities.

	35°	45°	54°
$\text{CH}_3\text{OH}$ .....	0.7781	0.7693	0.7615
$\text{C}_2\text{H}_5\text{OH}$ .....	0.7762	0.7678	0.7599

Dioxane was purified according to KURT HESS and HERMANN FRAHM (7). The commercial product was freed from water and

ethylene-acetal by prolonged boiling with thin slices of sodium and subsequent distillation from the sodium. Shaking with mercury showed the absence of peroxides, and the test for aldehydes with fuchsin-sulphuric acid was also negative.

### Apparatus.

A shaking apparatus according to BRØNSTED was used (Fig. 1). R is a glass-stoppered flask holding 75.5 ml. connected with a mercury manometer through the capillary g. The dead space

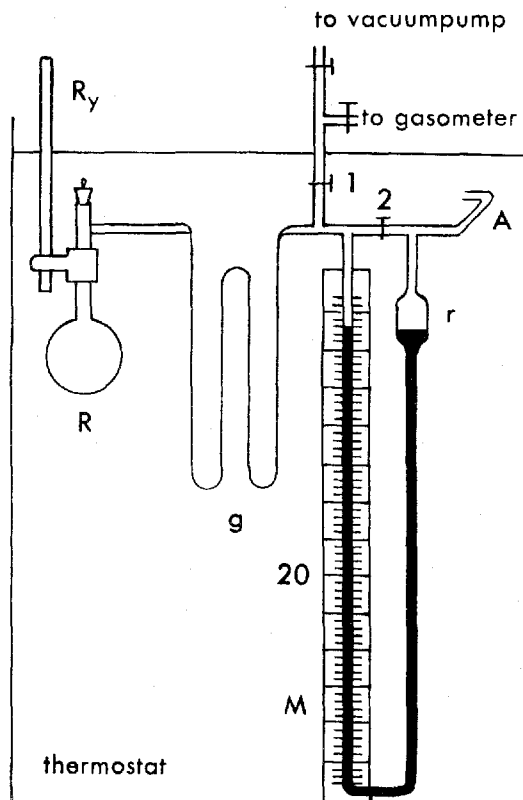


Fig. 1.

from the neck of the flask to the surface of the mercury in the left branch of the manometer is about 7.8 ml. It is essential to make this space as small as possible, since diffusion occurs at

the start of the experiment, giving rise to pressure variations which have nothing to do with the reaction itself. At A the tube bends backwards, connecting the mercury container r with a compensation flask behind R through a capillary similar to g. M is a milk glass scale graduated in millimeters; the manometer is read through a lens. R<sub>y</sub> is a shaking device carrying R and the compensation flask, so that both are shaken simultaneously. Through stopcock 1, the apparatus may be evacuated and filled with CO. Stopcock 2 serves to open between the two flasks and the two manometer branches (for evacuation) and to close it for filling R with CO. Obviously, this stopcock remains closed during the measurements. 1 and 2 are lubricated with a rather stiff grease capable of standing the highest temperatures used. The whole apparatus, including stopcocks 1 and 2, is kept in a thermostat, electrically heated and regulated to  $\pm 0.01^\circ$  in the usual manner by means of a toluene mercury regulator with relay. To avoid sparking, the current from the regulator is led to the grid of an ordinary triode radio valve whose anode current then actuates the relay. The temperature is read on a thermometer graduated in  $\frac{1}{10}$ th degrees, the readings of which are corrected by comparison with a standardized thermometer. Only the corrected temperatures are given in the tables. For time measurements, a stopwatch is used in slow experiments, and a wall clock sounding the minutes in fast ones.

### Procedure.

By means of a pipette, 22.00 ml. of catalyst solution (e. g., 1 molar sodium methylate in methanol) were transferred into the reaction flask (R), and 22 ml. of pure alcohol into the compensation flask. Stopcocks 1 and 2 were opened, and the apparatus was pumped until the liquids began to boil; subsequently, stopcock 1 was closed. If the pumping were continued, the concentration of the catalyst solution would be altered by evaporation.

The flasks were now shaken for about 10 minutes until the liquids had attained the temperature of the thermostat. Stopcock 2 was closed, and a portion of CO was let in through

stopcock 1, causing a depression of the manometer to, say, mark 20.

The shaking of the flasks was now resumed, the readings of time and pressure being started simultaneously; the manometer received a few taps before each reading. As the experiment progressed, the CO in the reaction flask was absorbed and the pressure decreased, as indicated by a rise of the mercury in the left branch of the manometer to about "mark zero".

Since the alcohol vapour pressure was eliminated by means of the compensation flask, the manometer recorded only the CO-pressure in the reaction flask.

Since the reaction proved to be of the first order, and it therefore seemed appropriate to apply GUGGENHEIM'S method (8) to the calculations, an initial set of readings was performed (column 2 of table 1) at definite times, which was followed by a second set of readings (column 3 of table 1) at the same time intervals, beginning at a given time (Z) after the start of the experiment. The time Z which is given in the table was always so chosen as to be of the order of magnitude of 2 to 5 times the half-time of the reaction.

After each experiment, 5.00 ml. of the cooled reaction mixture were titrated with 0.1 n HCl.

### Experimental data.

At each of the temperatures of about 35°, 45°, and 54°, experiments were made with approximately 1, 1/2, and 1/4 molar sodium methylate in methanol as well as with sodium ethylate in ethanol. At 54°, additional experiments were performed with approximately 1/2 molar concentrations of catalysts in a mixture of 50 % dioxane and 50 % alcohol.

All pressure readings were corrected according to the correction table given below, since it was found that blank experiments with pure alcohol in both flasks and CO excess pressure in flask R gave a reproducible small increase in pressure. Inasmuch as this increase did not follow a course of reaction of either the first or the second order, a blank experiment was carried out at each temperature, and the corrections obtained were subtracted from all pressures measured later.

In principle, objections can be raised to this method of correction, but the results obtained will nevertheless be substantially better than the uncorrected ones.

Originally, the corrections were much greater. However, after a re-dimensioning of the apparatus they became smaller. Unfortunately we have not succeeded in eliminating them altogether. The errors are probably caused by diffusion phenomena in the apparatus.

Correction Table.

Methanol					Ethanol					
P <sub>init.</sub>	35.05°	45.05°	45.05°	54.16°	P <sub>init.</sub>	35.05°	45.05°	54.16°	54.16°	54.16°
Min.	20 cm.	10 cm.	20 cm.	20 cm.	Min.	20 cm.	20 cm.	10 cm.	20 cm.	30 cm.
0	0	0	0	0	0	0	0	0	0	0
5	0.29	0.30	0.65	1.60	2	0.02	0.03	0.01	0.20	0.28
10	0.43	0.68	0.81	1.90	5	0.04	0.07	0.02	0.49	0.54
15	0.50	0.73	0.87	2.02	10	0.06	0.11	0.04	0.54	0.74
20	0.53	0.81	0.93	2.12	15	0.10	0.12	0.05	0.59	0.80
25	0.56	0.86	0.97	2.20	25	0.12	0.12	0.05	0.67	0.85
30	0.59	0.90	1.00	2.26	35	0.14	0.13	0.07	0.74	0.88
40	0.62	1.02	1.05	2.37	45	0.14	0.14	0.10	0.77	0.90
50	0.64	1.05	1.08	2.48	60	0.15	0.16	0.12	0.80	0.94
60	0.66	1.07	1.10	2.55	90	0.16	0.18	0.16	0.84	0.96
75	0.68	1.09	1.13	2.64	120	—	0.24	0.16	0.85	0.96
90	0.69	1.10	1.15	2.71	180	—	0.32	0.20	0.87	1.03
120	0.72	1.12	1.22	2.80	240	—	0.33	0.23	0.92	..
150	0.74	1.15	1.24	3.85	300	—	0.34	..	0.96	..
240	0.79	1.16	1.31	2.96	∞	..	0.51	..	..	..
300	0.80	1.16	1.32	3.00	..	..	..	..	..	..
∞	0.90	1.18	1.46	3.20	..	..	..	..	..	..

### Calculation of the experiments.

If the reaction is assumed to be of the first order, and  $k = -\frac{1}{t} \ln \frac{p-p_{\infty}}{p_0-p_{\infty}}$  is calculated for experiments 3, 4, and 14, 15, and 17 where the ratios of the initial pressures are 2/1 and 3/2/1, respectively, we find almost the same value for  $k$  when converting to the same concentration of catalyst. Thus, the reaction is in all probability of the first order, which is further



proved by the fact that  $k$  is almost constant throughout each experiment. A slight "drift" of the constant could, however, be demonstrated in almost all experiments,  $k$  first increasing, then reaching a maximum, and finally decreasing again. The maximum value was 1—4 % higher than the mean value.

It was assumed that all the time the shaking of the flasks was sufficiently effective to secure equilibrium between the CO in the gas phase and in the liquid phase.

The ester formed during the experiment has a low boiling point ( $\text{HCOOCH}_3$ : B. p.  $31.8^\circ$ ;  $\text{HCOOC}_2\text{H}_5$ : B. p.  $54.1^\circ$  at 1 atm.) so that considerable amounts of ester must pass over into the vapour phase. The pressure  $p$  read is thus the sum of the CO-pressure ( $p_{\text{CO}}$ ) and the ester pressure ( $p_{\text{E}}$ )

$$p = p_{\text{CO}} + p_{\text{E}}. \quad (1)$$

If only the velocity constants have to be calculated, the ester pressure causes no error in the calculation, as will be seen from the following considerations.

Since the ester concentration is small, its pressure must be proportional to its concentration in the solution, which again is proportional to the amount of CO absorbed. Consequently, at the time  $t$  we find

$$p_{\text{E},t} = a \cdot (p_0 - p_{\text{CO},t}), \quad (2)$$

where  $a$  is a proportionality factor,  $p_0$  the initial pressure of CO, and  $p_{\text{CO},t}$  the CO-pressure at the time  $t$ . Substituting (2) into (1) we find

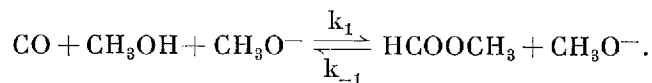
$$p = p_{\text{CO},t}(1 - a) + p_0a. \quad (3)$$

In addition, we have

$$p_\infty = p_{\text{CO},\infty}(1 - a) + p_0a \quad (4)$$

$$p - p_\infty = (p_{\text{CO},t} - p_{\text{CO},\infty})(1 - a) \quad (5)$$

As the reaction in solution, like the corresponding reaction in the gas phase, is assumed to be reversible, it follows



The alcohol concentration is almost constant because the alcohol is present in a large excess; furthermore, the concentration of catalyst is constant, and therefore it is not surprising that the reaction follows the unimolecular equation to which applies

$$\log (N_1 - N_{1,\infty}) = \log N \frac{k_1}{k_1 + k_{-1}} - (k_1 + k_{-1}) t \cdot \log e, \quad (6)$$

where  $N_1$  and  $N_2$  are the number of CO- and ester molecules, respectively,  $N_{1,\infty}$  the number of CO-molecules in the equilibrium state, and  $N_1 + N_2 = N$ .

Since, according to (5),  $N_1 - N_{1,\infty}$  is proportional to  $p - p_\infty$ , we find

$$\log (p - p_\infty) = -\text{constant}_1 \cdot t + \text{constant}_2,$$

i. e., the logarithm of the pressure difference decreases linearly with time; the ester pressure causes only a parallel displacement of the straight lines, their slopes give the velocity constant.

The calculation of the experiments was carried out according to GUGGENHEIM (8) with the modification that the proposed geometric method for the determination of  $k$  was replaced by a mathematical method proposed by J. A. CHRISTIANSEN (9). An example of this calculation is given in table 1 (experiment 11).

According to GUGGENHEIM's method,  $\log (p' - p)$  is plotted as ordinates and  $t$  as abscissae. A straight line is then drawn through the resulting points, and  $k$  is obtained from the slope of this line (cf. fig. 2).

However, the slope of the line may also be obtained by dividing differences in the logarithm with corresponding differences in time. This is most accurately done by extrapolating the value of  $\log (p' - p)$  at  $t = 0$  by plotting  $\log (p' - p)$  against  $t$  on a large scale; when drawing a straight line through the points obtained, the desired value is found as the point of intersection of the line with the log-axis (1.3500). Applying this and the following values of  $\log (p' - p)$ , the differences in column 6 were calculated successively. The corresponding time differences are in column 1. A series of  $k$ -values throughout the experiment was then obtained by calculating  $\frac{\Delta \log}{\Delta t}$ ; these values are recorded in column 7.

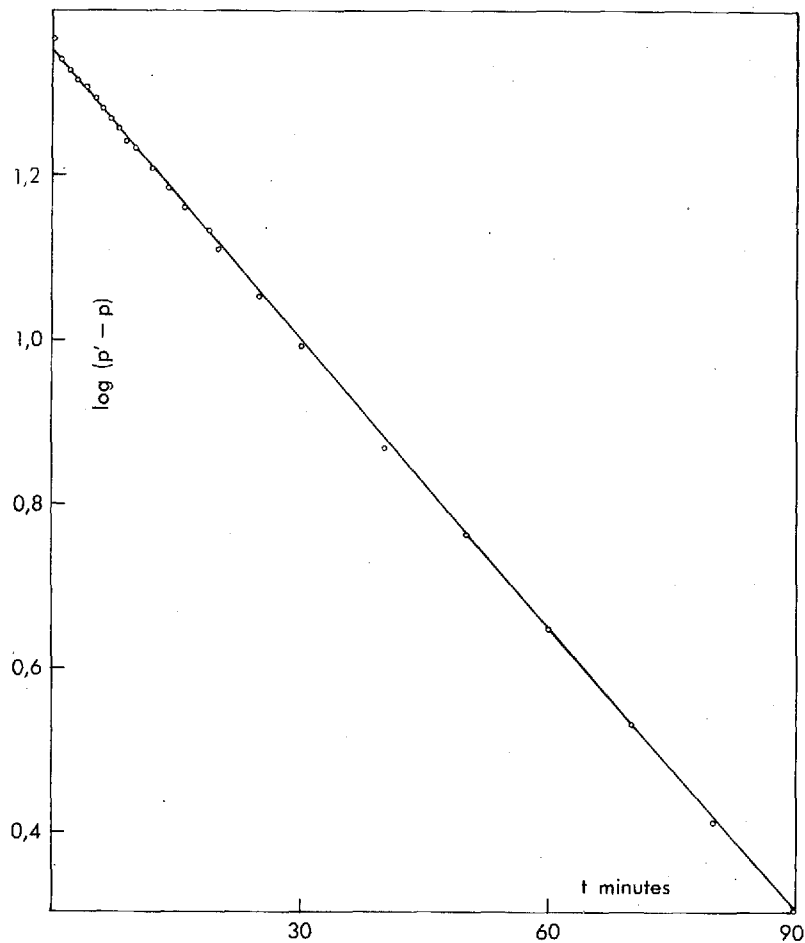


Fig. 2. The equation for the curve is  $\Delta \log (p' - p) = 11.74 \cdot 10^{-3} \cdot \Delta t$ .

According to J. A. CHRISTIANSEN (9), however, the most correct mean value of  $k$  is obtained by using the formula

$$k_{\text{mean}} = \frac{\sum G_i \cdot K_i}{\sum G_i},$$

where  $G_i$  denotes the statistical weight of the constant  $k_i$ .  $G_i$  (column 9) for the different stages (x) of a first order reaction is obtained from a table computed according to (9).

Practically, G which need not be particularly accurate, is read from a curve drawn on the basis of the values given in the table.

Table 1.  
Experiment 11. CO + 1.501 mol CH<sub>3</sub>ONa in CH<sub>3</sub>OH at 54.16°.

1	2	3	4	5	6	7	8	9
Min.	p	p'	p' - p	log (p' - p)	Δ log	k · 10 <sup>3</sup>	x	G <sub>i</sub>
0	17.90	41.19	23.29	1.3672 <sup>1</sup>	0		0	0
1	19.31	—23	21.92	1.3408	0.0092	9.2	0.06	0.20
2	20.03	—31	21.28	1.3280	0.0220	11.00	0.08	0.28
3	20.68	—40	20.72	1.3164	0.0336	11.20	0.11	0.38
4	21.22	—42	20.20	1.3053	0.0447	11.18	0.13	0.44
5	21.81	—47	19.66	1.2936	0.0564	11.28	0.15	0.50
6	22.41	—51	19.10	1.2810	0.0690	11.50	0.18	0.57
7	22.97	—55	18.58	1.2691	0.0809	11.56	0.20	0.61
8	23.53	—61	18.08	1.2572	0.0928	11.60	0.22	0.65
9	24.10	—65	17.55	1.2443	0.1057	11.74	0.24	0.68
10	24.64	—69	17.05	1.2317	0.1183	11.83	0.26	0.72
12	25.62	—78	16.16	1.2085	0.1415	11.79	0.30	0.75
14	26.59	—87	15.28	1.1841	0.1659	11.85	0.34	0.78
16	27.50	—94	14.44	1.1596	0.1904	11.90	0.38	0.80
18	28.36	—98	13.62	1.1331	0.2169	12.05	0.41	0.79
20	29.17	42.06	12.89	1.1103	0.2397	11.99	0.44	0.78
25	30.93	—20	11.27	1.0519	0.2981	11.92	0.52	0.72
30	32.52	—30	9.78	0.9904	0.3596	11.99	0.58	0.68
40	35.15	—53	7.38	0.8681	0.4819	12.05	0.68	0.51
50	36.96	—75	5.79	0.7627	0.5873	11.75	0.75	0.38
60	38.44	—88	4.44	0.6474	0.7026	11.71	0.81	0.25
70	39.59	—98	3.39	0.5302	0.8198	11.71	0.86	0.18
80	40.53	43.10	2.57	0.4099	0.9401	11.75	0.89	0.11
90	41.19	—20	2.01	0.3032	1.0468	11.63	0.92	0.07

Z = 1.5 hours.

$$\Sigma G = 11.63$$

$$\Sigma k \cdot G = 136.5078$$

$$k = \frac{136.5078}{11.63} = 11.74 \cdot 10^{-3} \text{ min.}^{-1}$$

<sup>1</sup> log (p' - p) extrapolated to t = 0 gives 1.3500.

Finally, we calculate  $\Sigma G = 11.63$  and  $\Sigma Gk = 136.5078$ , whereupon  $k_{\text{mean}}$  is found to be  $11.74 \cdot 10^{-3}$  (<sup>10</sup>logarithms, min.<sup>-1</sup>).

All k's are calculated according to the above described method.

The accuracy of the measured values of k is impaired for

different reasons. Owing to the high vapour pressure of the alcohols (cf. the table below), a slight difference in the temperatures of the reaction flask and the compensation flask causes an error of the pressure measured. At the most ( $\text{CH}_3\text{OH}$  at  $55^\circ$ ), a temperature difference of  $0.02^\circ$  between the two flasks will cause a pressure difference of 0.4 mm. Moreover, the correction mentioned on p. 7 may slightly falsify the results. The following alcohol vapour pressures given in cm Hg are interpolated on the basis of RICHARDSON'S results (10).

Temp.	$\text{CH}_3\text{OH}$	$\text{C}_2\text{H}_5\text{OH}$
$35^\circ$ . . . .	19.8	11.6
$45^\circ$ . . . .	38.4	17.6
$55^\circ$ . . . .	47.0	28.0

### Experimental results and discussion.

A survey of the experimental results is given in tables 2 and 3. The  $k$ -values are calculated on the basis of natural logarithms and seconds.

Table 2.  
Experiment with  $\text{CO} + \text{CH}_3\text{OH}$ ; catalyst  $\text{CH}_3\text{ONa}$ .

1	2	3	4	5	6	7	8
Expe- riment	Abs. temp.	$c_{\text{cat.}}$	$P_{\text{abs.}}$ cm. Hg	$k \cdot 10^5$ sec. $^{-1}$	$\frac{k \cdot 10^5}{c_{\text{cat.}}}$	$k^\circ 10^5$ sec. $^{-1}$	$k'' 10^5$ sec. $^{-1}$
6	308.15	1.004	27.70	7.25	7.25		
8	—	0.4181	18.95	2.16	5.16	4.15	11.3
7	—	0.2219	18.17	1.05	4.73		
3	318.15	0.9960	25.63	17.61	} 18.3		
4	—	—	11.09	18.76			
20a	—	0.5421	21.32	8.18	} 13.9	11.2	30.2
1	—	0.4403	25.10	5.69			
5	—	0.2201	24.00	2.82			
11	327.26	1.051	25.30	45.06	42.9		
9	—	0.4123	17.01	14.44	35.0	31.0	82.8
12	—	0.2207	19.47	7.33	33.2		

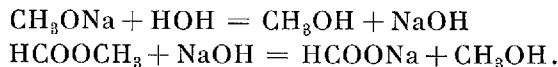
In the following experiment the reaction mixture contained 50 % dioxane.

26	327.26	0.4811	19.32	51.45			(286)
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Table 3.  
Experiment with CO + C<sub>2</sub>H<sub>5</sub>OH; catalyst C<sub>2</sub>H<sub>5</sub>ONa.

1	2	3	4	5	6	7	8
Experiment	Abs. temp.	c <sub>cat.</sub>	P <sub>abs.</sub> cm. Hg	k · 10 <sup>5</sup> sec. <sup>-1</sup>	$\frac{k \cdot 10^5}{c_{cat.}}$	k' · 10 <sup>5</sup> sec. <sup>-1</sup>	k'' · 10 <sup>5</sup> sec. <sup>-1</sup>
22	308.15	0.9976	19.87	16.33	16.4		
23	—	0.4972	21.97	7.14	14.3	12.8	34.8
24	—	0.2540	19.34	3.48	13.7		
19	318.15	0.9712	21.00	39.76	41.0		
20	—	0.4835	20.66	18.93	39.2	34.3	94.0
21	—	0.2369	20.89	8.31	35.0		
13	327.26	0.9616	20.46	88.62	97.1		
14	—	0.4837	34.53	41.76			
15	—	—	20.66	41.37	} 86.5	79.8	212
16	—	—	30.97	43.41			
17	—	—	11.97	41.03			
18	—	0.2434	19.56	20.20			
In the following experiment the reaction mixture contained 50 % dioxane.							
25	327.26	0.5187	21.30	118.8			(611)

After each experiment, 5.00 ml. of the reaction mixture were diluted with 50 ml. of CO<sub>2</sub>-free water and titrated with 0.1 n HCl; the ester concentrations found are recorded in table 4. After dilution, the following reactions take place:



The decrease in the quantity of base during each experiment must therefore be equivalent to the amount of ester formed, which again is equivalent to the amount of CO absorbed. The results which are summarized in table 4 show but a poor accuracy, partly because of the small amount of ester formed as compared to the catalyst concentration, and partly because of the volatility of the ester.

The above experiments prove that the reaction is of the first order with respect to CO. Moreover, at high dilution of CH<sub>3</sub>O<sup>-</sup>, the constant k is almost proportional to the concentration of CH<sub>3</sub>O<sup>-</sup>, increasing somewhat more rapidly at higher concentrations.

Presumably, we have here to do with some kind of salt

Table 4.

Experiment	CO <sub>abs.</sub> mmol	Ester formed mmol	$\frac{\text{mmol ester}}{\text{mmol CO}_{\text{abs.}}}$	
6	0.8659	0.754	0.87	CO + CH <sub>3</sub> O <sup>-</sup>
8	0.5924	0.577	0.98	
7	0.5680	0.505	0.89	
3	0.7761	0.781	1.01	
4	0.3470	0.324	0.93	
20 a	0.6456	0.686	1.06	
1	0.7600	0.638	0.84	
5	0.7267	0.797	1.10	
11	0.7451	0.817	1.10	
9	0.5033	0.510	1.02	
12	0.5734	0.546	0.95	
22	0.6211	0.680	1.09	
23	0.6868	0.714	1.04	
24	0.6045	0.633	1.05	
19	0.6359	0.678	1.07	
20	0.6256	0.683	1.09	
21	0.6325	0.678	1.07	
13	0.6025	0.523	0.87	
14	1.0169	1.029	1.01	
15	0.6084	0.573	0.94	
16	0.9121	0.878	0.96	
17	0.3407	0.360	1.05	
18	0.5670	0.575	1.00	

effect similar to what is known from the cane sugar inversion, where LEININGER and KILPATRICK (11) found the relation

$$\log \frac{k}{C_{\text{HCl}}} = \alpha + \beta \cdot C_{\text{HCl}}$$

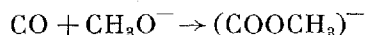
a relation which, incidentally, was found as early as in 1850 by WILHELMY (12).

An analogous relation seems to apply in our case; for data, cf. tables 2 and 3, column 6. By graphical extrapolation to  $c_{\text{CH}_3\text{O}^-} = 0$ ,  $k^0 = \frac{k}{c_{\text{cat.}}}$  was obtained, as recorded in tables 2 and 3, column 7.

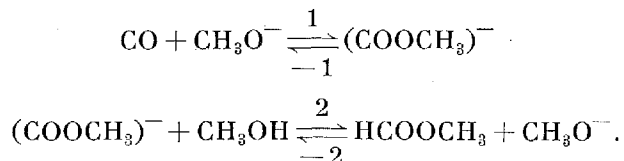
From the foregoing, it may be assumed that the velocity expression is

$$v = k \cdot c_{\text{CO}} \cdot c_{\text{CH}_3\text{O}^-}$$

and it follows that the velocity-determining reaction is



so that the complete reaction sequence becomes



However, only the existence of reaction 1 has been demonstrated directly or has been made probable by the experiments described. Since the stoichiometry of the reaction is known, the above stated reaction-sequence becomes the simplest one consistent with the experimental results. As early as in 1868, A. GEUTHER (13) showed that the decomposition reaction  $\text{HCOOCH}_3 \rightarrow \text{CO} + \text{CH}_3\text{OH}$  is also catalyzed by  $\text{CH}_3\text{O}^-$ .

The velocity constant  $k$  defined previously by the equation  $\frac{dp_{\text{CO}}}{dt} = -k \cdot p_{\text{CO}}$  depends, however, on the dimensions of the apparatus, since the reaction takes place in the liquid phase only. The velocity constant of the reaction in the liquid phase may be defined by the equation

$$\frac{dx}{dt} = k' \cdot c_{\text{CO}} \cdot c_{\text{cat.}}$$

where  $x$  is the amount of formate formed per litre of liquid;  $c_{\text{CO}}$  and  $c_{\text{cat.}}$  denote the concentration of CO and catalyst, respectively, in the liquid phase. Disregarding the vapour pressure of the formate, we find, however

$$-\frac{dx}{dt} = \frac{1}{RT} \cdot \frac{dp}{dt} \cdot \frac{V_g}{V_v},$$

where  $V_g$  and  $V_v$  are the volumes of the gas phase and the liquid phase, respectively, and

$$c_{\text{CO}} = \frac{p}{RT} \cdot \alpha,$$



where  $\alpha$  is the distribution coefficient of CO between the liquid and the gas phase. Consequently, we have

$$-\frac{dp}{dt} \cdot \frac{V_g}{V_v} = k' \cdot p \cdot \alpha \cdot c_{\text{cat.}}$$

from which

$$k' = k \cdot \frac{V_g}{V_v} \cdot \frac{1}{\alpha \cdot c_{\text{cat.}}} \rightarrow k^\circ \cdot \frac{V_g}{V_v} \cdot \frac{1}{\alpha}$$

i. e.  $\frac{k}{c_{\text{cat.}}} \rightarrow k^\circ$  when  $c_{\text{cat.}} \rightarrow 0$ .

The literature available contains no data on the solubility of CO in alcohols at temperatures as high as those of the present experiments; furthermore, an extrapolation would be too inaccurate owing to lack of data; it was therefore decided instead of  $k'$  to calculate  $k''$  defined by

$$k'' = k^\circ \frac{V_g}{V_v}$$

$k''$  is recorded in tables 2 and 3, column 8.

In order to get an impression of the "energy of activation" (4.571 A) and the "frequency exponent" (H), A and H were calculated from the equation

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

using the method of least squares. The figures obtained were for the reaction in methanol A = 4555, H = 10.82, and for the reaction in ethanol A = 4125, H = 9.93.

$k' = \frac{k''}{\alpha}$  should actually be used in the calculation of A and H. Applying the solubility data of G. Just (14) who determined the solubility of CO in methanol and ethanol at 20° and 25°, a and b were calculated for each reaction according to the formula  $\log \alpha = -\frac{a}{T} + b$ . In the case of methanol, the results were a = 501 and b = +0.97, which, subtracted from the previously calculated A- and H-values leads to A' = 4054 and H' = 9.85.

In the case of ethanol, the results were  $a = 78.64$  and  $b = -0.46$ , from which we find  $A' = 4046$  and  $H' = 10.39$ . However, the calculation of  $a$  and  $b$  is rather inaccurate, since the temperatures  $20^\circ$  and  $25^\circ$  lie so close together.

The apparent disagreement between A. STÄHLER's results and ours (cf. the introduction) may perhaps be explained by means

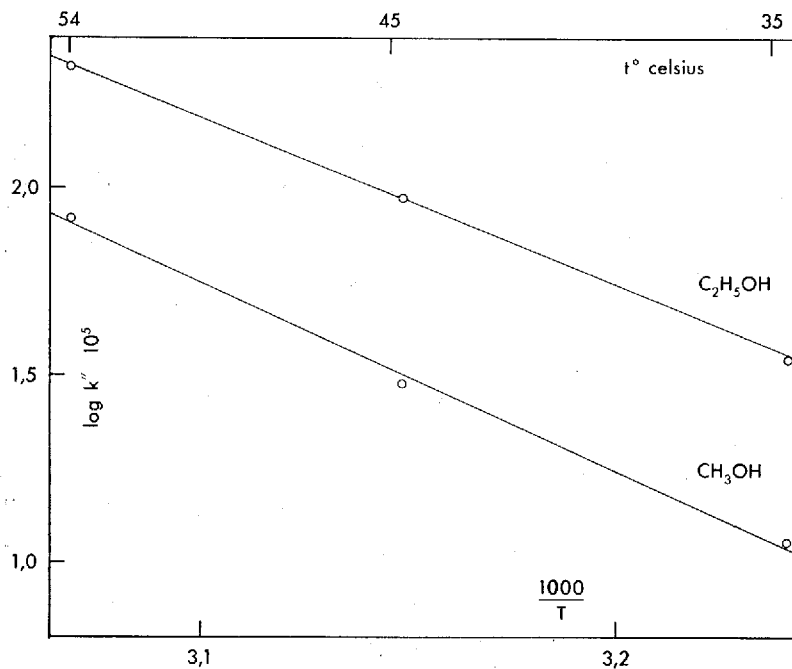


Fig. 3. The equation for the curve  $\text{CH}_3\text{OH}$  is  $\log k'' = -\frac{4555}{T} + 10.82$ ,  
the equation for the curve  $\text{C}_2\text{H}_5\text{OH}$  is  $\log k'' = -\frac{4125}{T} + 9.93$ .

of the calculated A- and H-values, as the curves for  $\log k$  intersect at about  $200^\circ$ . Consequently, above  $200^\circ$  the reaction in ethanol proceeds slower than in methanol, and it is faster below  $200^\circ$ , which might be in agreement with the observations by STÄHLER and by the present authors. However, this explanation seems somewhat uncertain, since the A-values used are only based upon three experiments within a small temperature interval ( $19^\circ$ ).

A calculation of the number of collisions  $S$  from the formula

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

where  $\sigma_{1,2}$  denotes the sum of the radii of the molecules,  $n$  the number of molecules per ml., and the  $M$ 's the molecular weights, leads to the following values at unit concentrations (1 mol/litre): For methanol  $H_{\text{calc.}} = \log S_1 = 11.22$ , and for ethanol  $H_{\text{calc.}} = \log S_2 = 11.14$ , where  $S$  is expressed in mol/litre per sec.

As radii of  $\text{CH}_3\text{O}^-$  and  $\text{C}_2\text{H}_5\text{O}^-$  are used the radii of  $\text{CH}_3\text{OH}$  and  $\text{C}_2\text{H}_5\text{OH}$ , respectively. The following values were applied:  $\sigma_{\text{CO}} = 1.6 \cdot 10^{-8}$  cm.,  $\sigma_{\text{CH}_3\text{OH}} = 2 \cdot 10^{-8}$  cm.,  $\sigma_{\text{C}_2\text{H}_5\text{OH}} = 1.8 \cdot 10^{-8}$  cm.,  $T = 318$ , and  $R = 8.32 \cdot 10^7 \frac{\text{erg.}}{\text{degr.}}$ .

Hence, the experimentally found values for  $10^H$  are not markedly different from the values calculated for the number of collisions (at unit concentrations) in the gas phase; this was found for many reactions in solution—cf., for example, LANDOLT BÖRNSTEIN'S tables (15)—and has been thoroughly discussed in the reaction-kinetic literature (TRAUTZ, LEWIS, and later authors).

Experiments 25 and 26 were performed in order to obtain information regarding the influence of the alcohol concentration on the velocity of the reaction. The initial solution in experiment 26 was 0.5 molar  $\text{CH}_3\text{ONa}$  in a mixture of equal parts of  $\text{CH}_3\text{OH}$  and dioxane; in experiment 25, 0.5 molar  $\text{C}_2\text{H}_5\text{ONa}$  in a mixture of equal parts of  $\text{C}_2\text{H}_5\text{OH}$  and dioxane.

The results are given in tables 2 and 3. In the methanol experiment, the velocity constant was about 3.6 times that of the corresponding experiment without dioxane, and in the ethanol experiment it was about 2.9 times as great. However, the greater velocity thus observed can hardly be due to the smaller alcohol concentration, but must be ascribed to the fact that the reaction now takes place in another medium.

In order to find whether CO reacts with a sodium hydroxide solution at low temperatures and pressures, an experiment was made analogous to those described above, using an approximately 1 molar NaOH solution at  $54.16^\circ$ .  $k$  of the reaction was found to be  $0.96 \cdot 10^{-5} \text{ sec.}^{-1}$ , which, giving due consideration to the solubility of CO in  $\text{H}_2\text{O}$  and the factor  $\frac{V_g}{V_v}$ , may be converted

into  $k' = 19.8 \cdot 10^{-4}$ . The corresponding constant of the methanol experiment at 1 molar  $c_{\text{cat}}$  is  $k' = 42.0 \cdot 10^{-4}$ . The velocity in water is thus about 2.1 times as slow as in methanol.

Our thanks are due to N. HOFFMANN-BANG, civil engineer, for valuable participation in the experiments.

### Summary.

1) The reaction between CO and  $\text{CH}_3\text{OH}$ , catalyzed by  $\text{CH}_3\text{ONa}$ , is investigated manometrically.  $\text{HCOOCH}_3$  is formed. The reaction is found to be of the first order with respect to CO. Its rate is shown to be determined by the reaction



the complex formed reacting to give  $\text{HCOOCH}_3$  and  $\text{CH}_3\text{O}^-$  which thus acts as a catalyst.

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

$$\log \frac{k}{c_{\text{cat}}} = \alpha + \beta \cdot c_{\text{cat}}. \quad (1)$$

3) Experiments with CO and  $\text{C}_2\text{H}_5\text{ONa}$  dissolved in  $\text{C}_2\text{H}_5\text{OH}$  proceed analogously, and here too, the relation between velocity constant and concentration is approximately described by equation (1). The velocity constant is about 3 times as great as for the reaction in  $\text{CH}_3\text{OH}$ .

4) Both series of experiments are carried out at approximately  $35^\circ$ ,  $45^\circ$ , and  $54^\circ$ . For the reactions in  $\text{CH}_3\text{OH}$  and  $\text{C}_2\text{H}_5\text{OH}$ , the energies of activation are both about 18500 small calories, respectively, and the frequency factors about  $10^{9.9}$  and  $10^{10.4}$ , respectively.

5) The reaction proceeds more rapidly if the solution contains dioxane.

6) The velocity constant for a reaction between CO and a solution of sodium hydroxide in water is of the same order of magnitude as the constants for the above reactions. However, the observed velocity is about 45 times smaller, mainly because CO is less soluble in water than in alcohol.

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Copenhagen, July 1942.

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