

The Kinetics of the Water Gas Conversion

II. Investigations at Elevated Pressures

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The validity of the rate equation previously found for the water gas conversion $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ over a commercial iron oxide-chromium oxide catalyst at atmospheric pressure has been investigated at elevated pressures and 380°C. It was found that the rate equation is satisfactorily obeyed up to at least 20 atm.

Data on the pressure dependence of the rate of the water gas conversion $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ are rather scarce in the literature. Atwood, Arnold and Appel¹ made their investigation under the assumption that a simple first order expression was valid. Atroshchenko and Bibr² also applied a kinetic expression quite different from ours.

In a previous article³ it was shown that the net rate of the water gas conversion over a commercial iron oxide-chromium oxide catalyst at atmospheric pressure in the temperature range 330–500°C could be adequately described by means of an expression of the exponential type

$$r = r_f - r_b = k (\text{CO})^l (\text{H}_2\text{O})^m (\text{CO}_2)^n (\text{H}_2)^q (1 - \beta) \quad (1)$$

where $\beta \equiv (\text{CO}_2)(\text{H}_2)/K(\text{CO})(\text{H}_2\text{O})$.

The exponents vary to some extent with temperature but were found to be situated between the following limits

$$0.80 \leq l \leq 1.00, \quad 0.20 \leq m \leq 0.35, \quad -0.65 \leq n \leq -0.50 \quad \text{and} \quad q = 0.$$

The present work was undertaken in order to investigate to which extent eqn. (1) is valid also at elevated pressures (up to 20 atm). The investigation has been performed at 380°C.

EXPERIMENTAL

Gases. All gases employed, CO , N_2 and CO_2 were taken from cylinders.

CO was about 98.5 % pure, the rest being mainly N_2 (about 1 %), H_2 (about 0.5 %), and O_2 (about 0.2 %). CO_2 was less than 0.1 %. Further, traces of iron carbonyl could be found whereas sulphur compounds and hydrocarbons could not be detected. CO was purified by passing over Cu-wire at 300°C (which removes oxygen and iron carbonyl),

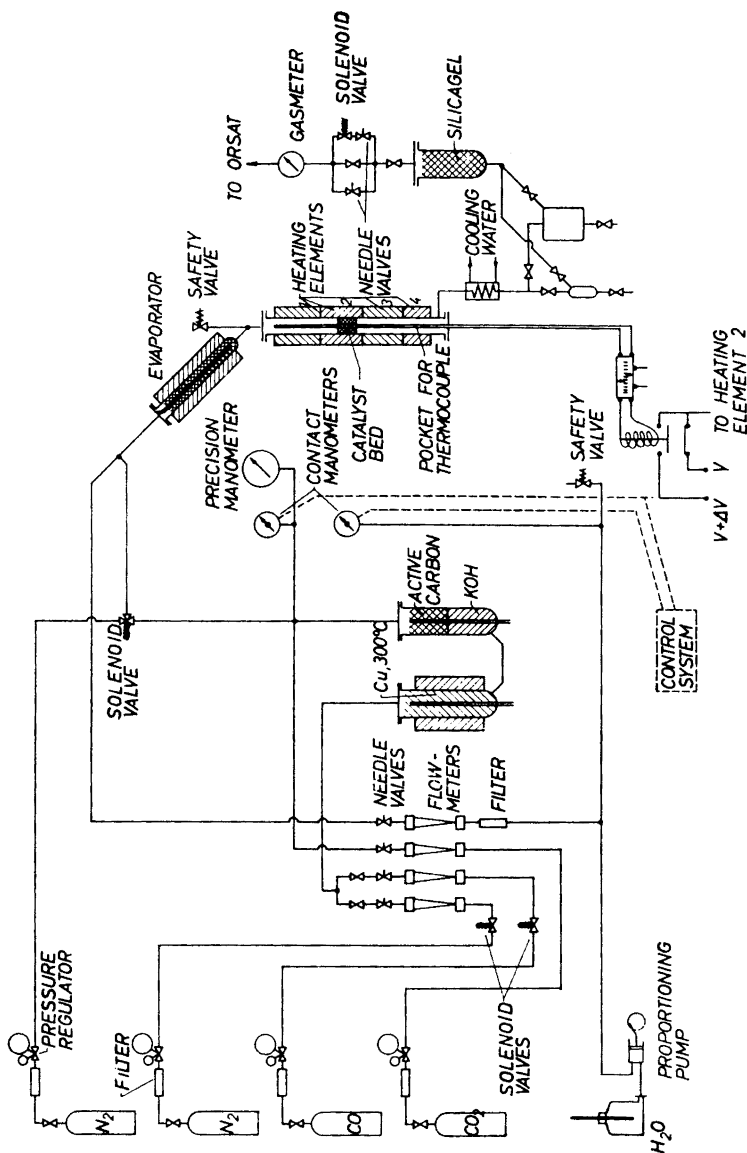


Fig. 1. Schematic drawing of experimental set-up.

alumina, potassium hydroxide pellets and active carbon. N_2 was purified in the same way whereas CO_2 was used without further purification.

Catalyst. The catalyst used was a commercial iron oxide-chromium oxide catalyst similar to the one used previously. Particle size was less than 0.5 mm. The amount of catalyst was 3.00 g (unreduced) diluted by 9.5 cm³ inert material (quartz) of approx. 1 mm particle size. The total volume of catalyst and diluting material was approx. 12 cm³. Before starting the measurements the catalyst was reduced and thereafter "aged" by running for about 2 weeks at 380°C and atmospheric pressure. Several different samples of somewhat varying activity have been applied for the investigation.

Experimental set-up. A diagram of the experimental set-up is shown in Fig. 1. The gases were supplied through flowmeters and, in the case of N_2 and CO, through a purification train, to the evaporator where liquid water was introduced by means of a proportioning pump. Mixture of water vapor and gases passed through the reactor containing a preheating zone and then the catalyst layer. The reactor consisted of a stainless steel tube which was heated by four sections of heating elements. A thermocouple tube passed through the catalyst layer so that the temperature could be measured at any level. The temperature of the catalyst layer was regulated by means of the thermocouple and a controller which regulated the voltage of heating element No. 2. After the reactor excess water was condensed and collected in containers (the larger one being used during the night) and the exit gas was dried by silica gel before relieving the pressure. The effluent gas passed through a gasmeter. Constant pressure was maintained automatically by means of a contact manometer for maximum pressure and a solenoid valve in series with an only slightly open needle valve at the exit side. The main stream of the exit gas passed through another needle valve. For the unattended operation during the night the set-up was provided with an automatic control system comprising a number of electronic relays, solenoid valves and a contact manometer for minimum pressure. If, e.g., the water pump would stop the CO stream would be shut off, the apparatus would be flushed with N_2 , and the electric current for the heating elements would be interrupted.

Analytical procedure. CO_2 was determined in an Orsat apparatus by absorption in KOH, thereafter CO was determined by oxidation with air over a CuO catalyst and subsequent absorption in KOH. H_2 was determined by gas chromatography. It was ascertained by gaschromatographic analysis that the exit gas did not contain essential amounts of CH_4 or other hydrocarbons at any of the pressures applied. When no CO_2 was included in the feed gas the degree of conversion was calculated on the basis of the CO and CO_2 found in the exit gas. If CO_2 was present in feed gas the H_2 content has been applied instead of the CO_2 content for the calculation of the degree of conversion.

LIST OF SYMBOLS

- F = total feed rate (mole/h).
 f = feed rate of CO (mole/h).
 k = pressure independent part of rate constant for forward reaction (defined by eqn. (1) or (2)).
 k_p = reaction rate constant for forward reaction at pressure p (defined by eqn. (3)).
 K = equilibrium constant for the water gas conversion.
 l, m, n and q = exponents occurring in the reaction rate eqn. (1).
 $(CO), (H_2O), (CO_2)$ and (H_2) = partial pressures (atm.) of CO, H_2O , CO_2 and H_2 , respectively.
 p = total pressure (atm.)
 r = net reaction rate (mole CO converted/(h)(g catalyst)).
 r_f and r_b = forward and backward reaction rates, respectively.
 W = weight of catalyst (g).
 x = degree of conversion of CO (mole CO converted/mole CO in feed gas).
 $y_{CO}, y_{CO_2}, y_{H_2O}$, and y_{H_2} = mole fractions of CO, CO_2 , H_2O and H_2 , respectively. Superscript zero indicates initial mole fraction.
 β = $(CO_2)(H_2)/K(CO)(H_2)$.
 γ = $y_{CO}, y_{H_2}/K y_{CO} y_{H_2O}$

THEORETICAL CONSIDERATIONS

Assuming eqn. (1) to be valid also at elevated pressure (with the same exponents) it is possible to substitute

$$(CO) = py_{CO}, (H_2O) = py_{H_2O}, (CO_2) = py_{CO_2}, \text{ and } (H_2) = py_{H_2}$$

Eqn. (1) is then replaced by

$$r = k \cdot p^{l+m+n+q} y_{CO}^l \cdot y_{H_2O}^m \cdot y_{CO_2}^n \cdot y_{H_2}^q (1-\gamma) \quad (2)$$

where $\gamma \equiv y_{CO} y_{H_2} / Ky_{CO} y_{H_2}$

Table 1. Variation of pressure. Approximate feed gas composition: CO : 16 %, CO₂ : 0 %, H₂ : 0 %, N₂ : 63 %, H₂O : 21 %.

No.	Total feed mole/h	Feed gas composition					Conv. exp. %	k_p	Pressure p atm. abs.
		% CO	% CO ₂	% H ₂	% N ₂	% H ₂ O			
1	3.671	15.80	0	0.06	64.64	19.50	21.8	0.0401	1.00
2	3.604	15.60	0	0.06	65.94	18.40	29.8	0.0708	1.98
3	3.804	15.30	0	0.06	63.14	21.50	39.8	0.124	4.88
4	3.783	16.40	0	0.06	61.54	22.00	51.4	0.225	9.69
5	3.700	17.20	0	0.06	61.24	21.50	59.5	0.330	19.39
6	3.750	16.60	0	0.06	61.94	21.40	50.8	0.221	9.71
7	3.746	16.60	0	0.06	62.34	21.00	42.3	0.148	4.87
8	3.838	15.40	0	0.06	64.84	19.70	29.1	0.0702	1.96

Table 2. Variation of pressure. Approximate feed gas composition: CO : 16 %, CO₂ : 0 %, H₂ : 0 %, N₂ : 51 %, H₂O : 33 %.

No.	Total feed mole/h	Feed gas composition					Conv. exp. %	k_p	Pressure p atm. abs.
		% CO	% CO ₂	% H ₂	% N ₂	% H ₂ O			
1	3.813	15.30	0	0.06	50.74	33.90	21.7	0.0348	1.00
2	3.808	16.40	0	0.06	50.84	32.70	27.5	0.0562	1.99
3	3.729	15.40	0	0.06	51.14	33.40	39.6	0.106	4.87
4	3.721	15.30	0	0.06	51.84	32.80	51.4	0.184	9.67
5	3.779	15.00	0	0.06	51.54	33.40	56.4	0.228	19.39
6	3.804	17.00	0	0.06	48.44	34.50	50.4	0.190	9.66
7	3.725	15.70	0	0.06	51.54	32.70	39.0	0.105	4.87
8	3.754	15.10	0	0.06	52.74	32.10	26.7	0.050	1.98
9	3.708	15.80	0	0.06	51.44	32.70	21.0	0.0329	1.00

Table 3. Variation of pressure. Approximate feed gas composition: CO : 16 %, CO₂ : 0 %, H₂ : 0 %, N₂ : 19 %, H₂O : 65 %.

No.	Total feed mole/h	Feed gas composition					Conv. exp. %	k_p	Pressure p atm. abs.
		% CO	% CO ₂	% H ₂	% N ₂	% H ₂ O			
1	3.821	15.30	0	0.06	18.64	66.00	31.5	0.0576	1.00
2	3.654	14.70	0	0.06	17.44	67.80	39.0	0.0805	1.96
3	3.721	15.70	0	0.06	18.74	65.50	49.1	0.139	4.89
4	3.675	16.00	0	0.06	19.64	64.30	56.9	0.194	9.72

Table 4. Variation of pressure. Approximate feed gas composition: CO : 40 %, CO₂ : 0 %, H₂ : 0 %, N₂ : 1 %, H₂O : 59 %.

No.	Total feed mole/h	Feed gas composition					Conv. exp. %	k_p	Pressure p atm. abs.
		% CO	% CO ₂	% H ₂	% N ₂	% H ₂ O			
1	3.750	40.10	0	0.16	0.84	58.90	23.0	0.0595	1.00
2	3.696	39.90	0	0.16	0.84	59.10	31.1	0.102	1.99
3	3.763	38.00	0	0.16	1.64	60.20	41.7	0.179	4.95
4	3.754	39.70	0	0.16	1.24	58.90	48.9	0.257	9.81

Table 5. Variation of pressure. Approximate feed gas composition: CO : 15 %, CO₂ : 33 %, H₂ : 0 %, N₂ : 18 %, H₂O : 34 %.

No.	Total feed mole/h	Feed gas composition					Conv. exp. %	k_p	Pressure p atm. abs.
		% CO	% CO ₂	% H ₂	% N ₂	% H ₂ O			
1	3.713	14.90	33.20	0.13	17.77	34.00	8.0	0.0722	1.00
2	3.658	14.90	33.30	0.13	17.97	33.70	11.2	0.101	2.04
3	3.775	15.50	33.00	0.13	17.37	34.00	17.6	0.171	4.95
4	3.767	15.40	32.60	0.13	16.77	35.10	24.3	0.246	9.75
5	3.879	14.20	33.40	0.12	19.08	33.20	32.7	0.379	19.66

Table 6. Variation of CO content in feed gas. Constant pressure of about 10 atm.

No.	Total feed mole/h	Feed gas composition					Conv. exp. %	k_p	Pressure p atm. abs.
		% CO	% CO ₂	% H ₂	% N ₂	% H ₂ O			
1	3.896	5.80	12.10	0.03	37.17	44.90	30.3	0.171	9.76
2	3.733	11.90	13.30	0.07	30.93	43.80	27.6	0.160	9.88
3	3.750	17.00	12.40	0.09	26.51	44.00	27.9	0.163	9.92
4	3.604	23.20	12.80	0.13	21.37	42.50	27.7	0.166	9.92
5	3.663	29.80	13.50	0.17	12.23	44.30	29.0	0.181	9.94

Table 7. Variation of CO₂ content in feed gas. Constant pressure of about 10 atm.

No.	Total feed mole/h	Feed gas composition					Conv. exp. %	k_p	Pressure p atm. abs.
		% CO	% CO ₂	% H ₂	% N ₂	% H ₂ O			
1	3.667	15.60	0	0.08	51.02	33.30	58.0	0.249	9.90
2	3.879	14.90	16.30	0.08	34.92	33.80	32.1	0.251	9.84
3	3.708	15.50	32.90	0.08	18.42	33.10	21.3	0.212	9.77
4	3.775	16.30	0	0.08	52.62	31.00	54.2	0.226	9.77

i.e., if eqn. (1) is valid also at elevated pressure (with pressure independent exponents) a plot of $\ln p$ against the logarithm of an experimental rate constant k_p evaluated from the equation

$$r = f \cdot (dx/dw) = k_p \cdot y_{\text{CO}}^l \cdot y_{\text{H}_2\text{O}}^m \cdot y_{\text{CO}_2}^n \cdot y_{\text{H}_2}^q (1-\gamma) \quad (3)$$

should yield a straight line with the slope $= l + m + n + q$.

The next question which arises is: if a linear relationship between $\ln k_p$ thus determined and $\ln p$ is obtained, does that mean that l , m , n and q are independent of pressure. It is conceivable if only a single series of runs with varying pressure and constant feed gas is made that l , m , n , and q may vary in such a manner that a straight line with slope equal to that calculated from the atm. pressure equation is obtained. If, however, a linear relationship between $\ln k_p$ and $\ln p$ is obtained with several feed gases and particularly with a feed gas containing an essential amount of CO_2 as well as with a feed gas without CO_2 it can be concluded that l , m , n and q are at least approximately independent of pressure within the interval investigated.

EVALUATION OF EXPERIMENTAL RESULTS

The procedure for obtaining the experimental data for the evaluation of the relation between $\ln k_p$ and $\ln p$ has been the following. A series of runs has been made by maintaining a fixed space velocity, feed gas composition and temperature (380°C) and then varying the pressure from 1 to 10 or 20 atm. This procedure has been repeated with other feed gas compositions. In order to determine the exponents l and n independently two series of runs have also been made at the constant pressure of 10 atm. at varying concentrations of CO and CO_2 , respectively, in the feed gas (*cf.* Ref.³).

From the experimentally found conversions the rate constant k_p has in each case been evaluated by integration of eqn. (3) by means of the electronic digital computer DASK after insertion of the appropriate values of l , m , n and q . In the previous work³ it was found that the values of the exponents l , m , n and q at 380°C and atmospheric pressure were $l = 1.00$, $m = 0.20$, $n = -0.65$ and $q = 0$; *i.e.* $l + m + n + q = 0.55$. From the preliminary calculations it appeared, however, that a better average value of the slope than 0.55 would be 0.65. This difference is definitely within the experimental uncertainty as each of the exponents is subject to an uncertainty of at least 0.05. In order to obtain the slope 0.65 it seemed the most logical to change the value of m to 0.25 and the value of n to -0.60 . The new value of m is actually in better accordance with the values obtained at the neighbouring temperatures 330° and 420° at atmospheric pressure than the previous one (*cf.* Ref.³).

By inserting in eqn. (3) these values of the exponents,

$$f = y_{\text{CO}}^3 \cdot F, \quad y_{\text{CO}} = y_{\text{CO}}^c (1-x), \quad y_{\text{H}_2\text{O}} = y_{\text{H}_2\text{O}}^c - x \cdot y_{\text{CO}}^c, \quad \text{and} \quad y_{\text{CO}_2} = y_{\text{CO}_2}^c + x \cdot y_{\text{CO}}^c$$

we obtain the following eqn. from which the values of k_p have been determined.

$$F \cdot (dx/dw) = k_p \cdot (1-x) (y_{\text{H}_2\text{O}}^c - x \cdot y_{\text{CO}}^c)^{0.25} (y_{\text{CO}_2}^c + x \cdot y_{\text{CO}}^c)^{-0.60} (1-\gamma) \quad (4)$$

The technique applied for obtaining k_p has been a little different from that described previously³. By application of an arbitrary (approximate) rate

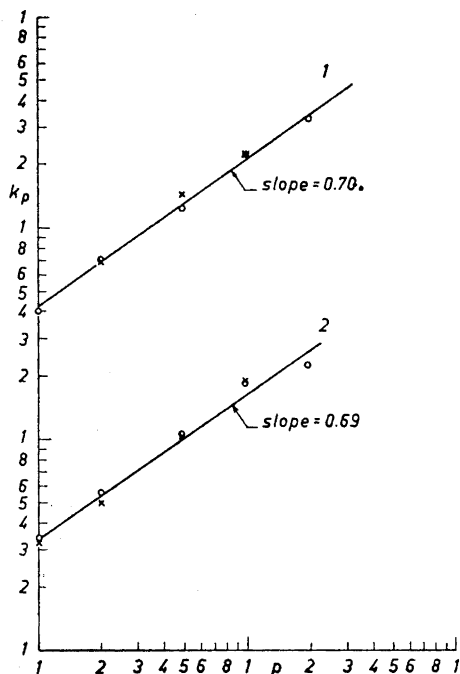


Fig. 2. Plot of $\ln k_p$ vs. $\ln p$. Data from Tables 1 and 2. \circ — \circ : increasing pressure, \times — \times : decreasing pressure. Numbering of the lines corresponding to that of the tables. Ordinate of line 1 displaced one decade relatively to that of line 2.

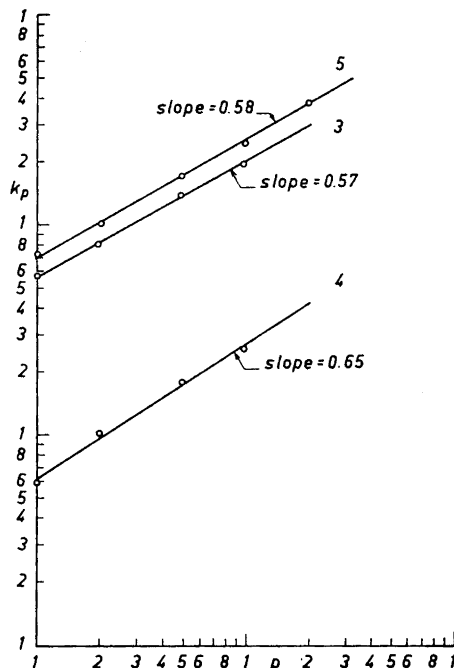


Fig. 3. Plot of $\ln k_p$ vs. $\ln p$. Data from Tables 3, 4 and 5. Numbering of the lines corresponding to that of the tables. Ordinate of line 4 displaced one decade relatively to that of lines 3 and 5.

constant k_p^* the integration is performed through a catalyst layer of such length that the calculated exit gas composition is equal to the experimentally found exit gas composition. From the amount of catalyst, W^* , thus obtained k_p is calculated from the relation $k_p \cdot W = k_p^* \cdot W^*$ in which W is the actual amount of catalyst.

Table 8. Slopes obtained from the plots of $\ln k_p$ vs. $\ln p$. (Figs. 2 and 3).

Approximate feed gas composition	Pressure range applied	Slope	Line No.
16 % CO, 0 % CO ₂ , 0 % H ₂ , 63 % N ₂ , 21 % H ₂ O	1–20 atm.	0.70	1
16 % CO, 0 % CO ₂ , 0 % H ₂ , 51 % N ₂ , 33 % H ₂ O	1–20 atm.	0.69	2
16 % CO, 0 % CO ₂ , 0 % H ₂ , 19 % N ₂ , 65 % H ₂ O	1–10 atm.	0.57	3
40 % CO, 0 % CO ₂ , 0 % H ₂ , 1 % N ₂ , 59 % H ₂ O	1–10 atm.	0.65	4
15 % CO, 33 % CO ₂ , 0 % H ₂ , 18 % N ₂ , 34 % H ₂ O	1–20 atm.	0.58	5

The experimental conditions and the experimentally found conversions together with the values of k_p thus obtained are given in Tables 1–7. The hydrogen appearing in the feed gas originates from that contained in the CO feed gas. The balance gas is listed in the tables as N_2 . Figs. 2 and 3 show the plots of $\ln k_p$ vs. $\ln p$. The slopes obtained from these plots are summarized in Table 8.

DISCUSSION

The question of diffusion restriction has been discussed in the previous article³ and with the particle size being smaller in the present case it is concluded that the influence of diffusion restriction is again negligible. On the other hand it may be pointed out that for catalyst pellets of industrial sizes (e.g. 9 mm) the pressure dependence of the rate of reaction will ordinarily be essentially influenced by diffusion restriction, and the present results therefore in such cases not directly applicable without correction factors.

It appears from the figures that $\ln k_p$ to a good approximation is linearly dependent upon $\ln p$ in the pressure range 1 to 10 or 20 atm. and that the slope of the straight line is approximately that which should be expected on the basis of the rate equation obtained at atmospheric pressure. The minor variation of the slope (from 0.57 to 0.70) may be at least partly due to experimental uncertainty; there is, however, some indication that an increase of the ratio of $H_2O:CO$ causes a decrease of the slope in a CO_2 -free feed gas and that a content of CO_2 in feed gas also lowers the slope. There is no clear indication of a deviation from linearity even at the highest pressures applied (approx. 20 atm.). It should be mentioned that application of erroneous values of l , m , n and q for the calculation of the rate constant k_p has only a slight influence on the slope obtained as long as the errors in the exponents are not exceedingly large. Particularly the influence of minor errors in l and m (and in n when CO_2 is present in feed gas) is completely negligible.

Table 6 shows the results of a series of runs at 10 atm with varying CO content in feed gas. The constancy of k_p , obtained by application of eqn. (4) shows that the value of $l = 1.00$ is also valid at this pressure. Table 7 gives a few runs with varying CO_2 content in feed gas. The k_p 's calculated from these do not contradict the value of $n = -0.60$.

In conclusion it may be said that the present results largely confirm the results obtained at atmospheric pressure and further that the same rate equation is valid at total pressures up to about 20 atm.

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REFERENCES

1. Atwood, K., Arnold, M. R. and Appel, E. G. *Ind. Eng. Chem.* **43** (1950) 1600.
2. Atroshchenko, V. J. and Bibr, B. *Zhur. Priklad. Khim.* **32** (1959) 997; *Chem. Abstr.* **53** (1959) 15735.
3. Bohlbro, H. *Acta Chem. Scand.* **15** (1961) 502.

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