

The Rate of Oxidation of Carbon Monoxide in Presence of Nitrogen Dioxide

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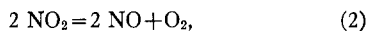
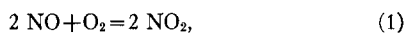
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The Rate of Oxidation of Carbon Monoxide in Presence of Nitrogen Dioxide

The effect of nitrogen dioxide has been studied by Crist and Roehling.¹ They suggested that the reaction had a complicated chain mechanism for low concentrations of nitrogen dioxide and that it was homogeneous for larger amounts of the catalyst.

We have studied the reaction in Pyrex, quartz, aluminum, and Pyrex treated with a potassium chloride solution. It was found that the reaction for low nitrogen dioxide pressures (0.06–5 mm) was greatly affected by the surface volume ratio and by the material of the reaction vessel. The rate was comparatively small in the Pyrex vessel washed with a potassium chloride solution. At higher pressures of nitrogen dioxide the reaction was unaffected by the nature of the vessel.

The homogeneous portion appears to consist of the reactions:



The experimental method was varied so as to isolate these reactions. In a mixture with the approximate concentrations, total nitrogen dioxide = 10 mm, oxygen = 600 mm, and carbon monoxide = 50 mm, the reaction was found to be first order with respect to both carbon monoxide and nitrogen dioxide and proportional to the square root of the oxygen pressure. When the oxygen concentration is large it would be practically constant and the rate would be expressed by

$$-\frac{d\text{CO}}{dt} = k_3[\text{NO}_2][\text{CO}].$$

Then, in order to obtain k_3 we calculate the nitrogen dioxide on the assumption that it is constant at the equilibrium concentration. The values of k_3 at 385°C and 527°C are, respectively, $1.12 \times 10^2 (\pm 0.07) \text{ sec}^{-1}$ and $8.50 \times 10^3 (\pm 0.20) \text{ sec}^{-1}$.

In order that reaction (1) should determine the rate, the mixture taken was approximately as follows: nitrogen dioxide = 10 mm, carbon monoxide = 600 mm and oxygen = 20 mm. Since the oxygen pressure is low the nitrogen dioxide concentration will also be small and the amount of

nitrogen dioxide lost by reaction (2) will be relatively small. The results show that the reaction under these conditions is first order with respect to oxygen, independent of the carbon monoxide, and proportional to the square of the nitric oxide when its concentration is not too large. This is in accordance with the equation

$$-\frac{d\text{O}_2}{dt} = k_1[\text{NO}]^2[\text{O}_2].$$

The results are in Table I.

TABLE I. Rate constants for the oxidation of nitric oxide.

Temperature = 385°C		Temperature = 527°C	
Pressure in mm of NO (Total)	$k_1 \times 10^{-9}$ cc ² mole ⁻² sec. ⁻¹	Pressure in mm of NO (Total)	$k_1 \times 10^{-9}$ cc ² mole ⁻² sec. ⁻¹
6.80	2.02	7.37	4.21
10.0	2.05	7.65	4.37
11.5	1.80	10.8	4.20
15.4	1.48	13.4	3.92
17.4	1.47	15.7	3.38
25.2	0.79	15.8	3.37
		16.0	3.45
		19.0	3.68
		28.0	2.47

The decrease of the rate constant at higher nitrogen dioxide pressures could be due to increased nitrogen dioxide decomposition. The best value for k_1 would then be that obtained at the lower concentration of nitrogen dioxide. The value of the constant at 385°C is in fairly good agreement with the work of Bodenstein.² The constant at 527°C is in accordance with the predictions that the temperature coefficient should become positive at temperatures above 400°C.

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¹ Crist and Roehling, J. Am. Chem. Soc. **57**, 2196 (1935).

² Kassel, *Kinetics of Homogeneous Gas Reactions* (Chemical Catalog Co., 1932), p. 157.