Rate and Adsorption Constants of Oxidation Reaction of Hydrogen Chloride

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In a previous paper (*1*) it was reported that the data for the catalytic oxidation of hydrogen chloride over chromic oxide catalyst were well correlated by the following Hougen-Watson type of rate equation:

$$r = \frac{k\left[p_A^{1/2} - \left(\frac{p_C p_D}{p_B^2 K(T)}\right)\right]}{1 + \beta p_B + \gamma p_C + \frac{\alpha p_C p_D}{p_B^2 K(T)}} \qquad (1)$$

The adsorption equilibrium constants of oxygen, hydrogen chloride, and water, which were estimated at three different temperature levels, exhibited abnormal behavior with temperature; all these constants increased with rising temperature. For this reason the constants α, β, and γ in Equation (1) were considered to be empirical constants and not adsorption equilibrium constants. As described in an earlier paper, these rate constants were estimated by means of linear least squares method which was applied on the linearized form of Equation (1).

As reported by Kittrell and co-workers (*5*), it would be advantageous to employ nonlinear least squares procedures to estimate parameters with which rate equation may describe *all* the data adequately. Thus, in an attempt to reexamine the constants previously estimated and also to avoid the errors inherent in these estimation procedures, the equation was fitted to the original rate data of Jones (*4*) at all the temperature levels simultaneously by nonlinear least squares (*2*, *3*). For this purpose Equation (1) was rewritten as

$$r = \frac{\exp(-\Delta H_k/RT + \Delta S_k/R)\left[p_A^{1/2} - \left(\frac{p_C p_D}{p_B^2 K(T)}\right)\right]}{1 + \exp\left(\frac{\Delta H_\beta}{RT} - \frac{\Delta S_\beta}{R}\right)p_B + \exp\left(\frac{\Delta H_\gamma}{RT} - \frac{\Delta S_\gamma}{R}\right)p_C + \exp\left(\frac{\Delta H_\alpha}{RT} - \frac{\Delta S_\alpha}{R}\right)\frac{p_C p_D}{p_B^2 K(T)}} \qquad (2)$$

The resulting best estimates of parameters in Equation (2) are shown in Table 1. The agreement between ΔH_k and the originally reported activation energy of 58,000 cal./g.-mole should be noted. The signs of ΔH and ΔS agree with the usual predictions of heterogeneous kinetic theory and of chemisorption processes. The best estimates of the constants α, β, and γ (previously considered to be empirical) now decrease as temperature rises and thus may be considered as adsorption equilibrium constants K_A, K_B, and K_C. Estimates of the pure error mean square were not available due to lack of reliable replicated experimental data. Thus the method of testing lack of fit was not applied for the justification of the adequacy of the proposed model. However, the residuals of reaction rates were randomly distributed. Thus it may be concluded that the model described by Equation (2) could be an adequate model for the catalytic oxidation of hydrogen chloride within the experimental region employed.

TABLE 1. PARAMETER ESTIMATES FOR EQUATIONS (1) AND (2)

	ΔH, cal./g.-mole	ΔS, cal./(g.-mole) (°K.)
k	57,560	74.94
K_A	8,286	1.09
K_B	600	0.38
K_C	3,200	0.50

NOTATION

ΔH_k, ΔH_α, ΔH_β, ΔH_γ = enthalpy change for reaction rate, adsorption of oxygen, hydrogen chloride, and water, cal./g.-mole
k = reaction rate constant for adsorption step rate controlling, g.-moles oxygen/(g.-catalyst)(min.)/atm.$^{1/2}$
K_A = adsorption equilibrium constant of oxygen, atm.$^{-1/2}$
K_B, K_C = adsorption equilibrium constant of hydrogen chloride and water, atm.$^{-1}$
$K(T)$ = homogeneous gas phase equilibrium constant, atm.$^{-1/2}$
p_A, p_B, p_C, p_D = partial pressure of oxygen, hydrogen chloride, water, and chlorine, atm.
r = rate of reaction, g.-moles oxygen/(g.-catalyst)(min.)
R = gas constant 1.98 cal./(g.-moles)(°K.)
ΔS_k, ΔS_α, ΔS_β, ΔS_γ = entropy change for reaction rate, adsorption of oxygen, hydrogen chloride, and water, cal./(g.-moles)(°K.)
T = temperature, °K.
α = same as K_A, originally regarded as empirical constant, atm.$^{-1/2}$
β, γ = same as K_B and K_C, originally regarded as empirical constant, atm.$^{-1}$

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