1 : 1 Complexes of Acid Chromate Ion with Alcohols or Acetaldehyde

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Evidence for 1:1 complexes of acid chromate ion with some aliphatic alcohols or acetaldehyde is presented. The stability constants and spectra have been measured, and the heat of formation of one of the complexes (the 2-propanol complex) has been determined. In view of these complexes, the light sensitiveness of the acid chromate-alcohol solutions will be discussed.

Westheimer *et al.*¹⁻³ have investigated the kinetics of the oxidation of 2-propanol to acetone by acid chromate ions in aqueous solution, and have shown that the primary step in the reaction is the formation of a complex (an ester)

Edwards has postulated the existence of a similar complex⁴.

At low acidities, 10^{-2} M to 10^{-3} M, and temperatures below 40°C , the above mentioned oxidation is extremely slow. Under these conditions the present author has found evidence for an equilibrium of the type:

where X stands for an alcohol or acetaldehyde. In more acid solutions these complexes (probably esters) may react with a proton to form unstable complexes (esters) similar to those proposed by Westheimer.

Measurements were made of the difference in extinction $\Delta\epsilon$ of two solutions, both containing 10^{-4} M acid chromate and 10^{-3} M perchloric acid, one of them, furthermore, an alcohol or acetaldehyde. Under these conditions less than 1 % of the acid chromate is present as dichromate. For constant alcohol concentration $\Delta\epsilon$ was measured at wavelengths between $260\text{ m}\mu$ and $420\text{ m}\mu$; at $375\text{ m}\mu$ $\Delta\epsilon$ was measured at various concentrations of alcohol or acetaldehyde.

Figure 1. $\Delta\epsilon/c_a$ versus $\Delta\epsilon$ for acid chromate solutions containing 1) methanol, 2) ethanol, 3) *n*-propanol, 4) 2-propanol, 5) 2-butanol and 6) acetaldehyde.

Figure 2. The absorption spectrum of the acid chromate ion 0), and the absorption spectra of the complexes of acid chromate with 1) methanol, 2) ethanol, 3) *n*-propanol, 4) 2-propanol, 5) 2-butanol and 6) acetaldehyde.

The following relation was established, indicating the existence of a 1:1 complex:

$$\frac{\Delta\epsilon}{c_a} = K \cdot \Delta\epsilon_{K1} \cdot l \cdot c_0 - K \cdot \Delta\epsilon$$

where K is the stability constant, l the length of the optical path in cm, c_a the concentration of alcohol or acetaldehyde, c_0 the concentration of acid chromate, and $\Delta\epsilon_{K1}$ the difference between the extinction coefficient of the complex and that of the acid chromate ion at 375 $m\mu$.

From the straight line representing $\Delta\epsilon/c_a$ as a function of $\Delta\epsilon$, K and $\Delta\epsilon_{K1}$ were calculated for methanol, ethanol, *n*-propanol, 2-propanol, 2-butanol and acetaldehyde (Fig. 1). The stability constants in litre $\cdot$ mole $^{-1}$ at 25°C were, for methanol 0.043, ethanol 0.077, *n*-propanol 0.109, 2-propanol 0.078, 2-butanol 0.082 and for acetaldehyde 0.034. The spectra were obtained from measurements of $\Delta\epsilon$ at varying wavelengths, knowing the absorption spectrum of the acid chromate ion⁵. The spectra of the complexes are shown in Fig. 2.

The equilibrium constant for 2-propanol was measured also at 11°C, 0.0884, and at 35°C, 0.0746, giving a value for the heat of formation of $-\Delta H = 1.31$ kcal/mole.

Furthermore it was found that $\Delta\epsilon$ is independent of the concentration of perchloric acid in the interval 2×10^{-4} — 0.2 M, indicating that the complexes, like the acid chromate ion, are weak both as acids and as bases. At the highest acidities the oxidation is rather fast, $\Delta\epsilon$ therefore was found by extrapolating $\log \epsilon$ to zero time, assuming a first order reaction rate.

Westheimer¹ has found that the dichromate ion is inactive in the above mentioned oxidation. In agreement with this, measurements of the extinction per cm, ϵ , at 366 m μ of solutions containing dichromate and 2-propanol indicated that the interaction between 2-propanol and dichromate ions is weak. In these experiments the concentration of 2-propanol was 3 M, the ionic strength was 10^{-2} and the total chromium concentration c_0 was varied between 5×10^{-4} M and 1.5×10^{-3} M. Assuming that the dichromate ion does not form a complex with 2-propanol, we may write for the extinction ϵ :

$$\epsilon = \epsilon_1 \cdot c_0 + 2c_2\Delta\epsilon_{21} + c_K\Delta\epsilon_{K1}$$

where ϵ_1 is the extinction coefficient of acid chromate and $\Delta\epsilon_{21}$ the difference between the extinction coefficient of dichromate and that of acid chromate. c_2 and c_K are concentrations of dichromate and of the complex, respectively. c_K is given by:

$$2c_K^2K_2 + c_K(K \cdot c_a + K^2c_a^2) - K^2c_a^2c_0 = 0$$

c_2 is given by

$$4K_2c_2^2 - (1 + 4K_2(c_0 - c_K))c_2 + (c_0 - c_K)^2K_2 = 0$$

where K_2 is the constant for the equilibrium between acid chromate and dichromate. From these equations ϵ has been calculated. For $\Delta\epsilon_{K1}$ and K the values at $c_0 = 10^{-4}$ M have been used. $\Delta\epsilon_{21}$ is known⁶, 873 litre·mole⁻² cm⁻². K_2 has been determined by Tong and King⁷, $K_2 = 45$ litre·mole⁻¹. Table 1 shows the calculated and the measured values of ϵ at various concentration c_0 .

Table 1. 25.0°C

c_0 mole/litre	ϵ measured	ϵ calculated
1.5×10^{-3}	2.445	2.462
1.0×10^{-3}	1.632	1.623
7.5×10^{-4}	1.210	1.215
5.0×10^{-4}	0.805	0.807

We introduce the coefficient $\gamma_0 = \frac{c_a \cdot K \cdot \epsilon_K}{c_a \cdot K \cdot \epsilon_K + \epsilon_1}$, where ϵ_K is the extinction coefficient of a complex. γ_0 is that fraction of the absorbed photons, which are absorbed by the complexes. At small values for c_a , γ_0 becomes $\frac{c_a \cdot K \cdot \epsilon_K}{\epsilon_1}$

In Table 2 the γ_0/c_a values at 366 m μ are given for the 5 alcohols and acetaldehyde. The quantum yields for the photochemically induced oxidation of some of the above mentioned alcohols and acetaldehyde by acid chromate at 366 m μ have been determined by Bowen and Chatwin⁸. Their values for the quantum yields

Table 2. 25.0°C

Complex	γ_0/c_a	γ/c_a
Acetaldehyde-	0.065	0.0396
Methanol-	0.079	0.0130
Ethanol-	0.155	0.0416
<i>n</i> -Propanol-	0.217	0.0470
2-Propanol-	0.179	0.0470
<i>n</i> -Butanol-	—	0.081
2-Butanol-	0.220	—
Isobutanol-	—	0.0775

in dilute solutions divided by the alcohol or acetaldehyde concentrations, γ/c_a , are also given in Table 2. We note that γ_0/c_a varies parallel to γ/c_a (except for acetaldehyde), suggesting that it is the complexes, which are photochemically active.

EXPERIMENTAL

Acetaldehyde was distilled just before use. The alcohols were purified by distillation. The normal alcohols were distilled over NaOH and $\text{Pb}(\text{CH}_3\text{COO})_2$ to remove aldehydes. The solutions were made with redistilled water.

The extinction measurements were made with a Beckman DU spectrophotometer. The temperature was held within 0.2°C by circulating thermostated water through the Beckman Thermospacer.

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Received May 17, 1957.