A comparison of the experimental results for ketonization with the theoretical curves permits a choice of the model for the ketonization reaction.

This method, however, has its limitations. The reactant involving two of its molecules must be able to undergo a competitive reaction with another substrate. If the ratio of the adsorption coefficient of the original reactant to the competing reactant is less than 3 according to the Langmuir-Hinshelwood model for the esterification, the theoretical plots for the two mechanisms do not differ sufficiently to permit an unambiguous choice.

Isopropyl alcohol and methyl alcohol form esters with acetic acid and therefore compete with the ketonization reaction. The adsorption coefficient of acetic acid relative to isopropanol from the Langmuir-Hinshelwood model for esterification is less than 3 and the results plotted in Fig. 1 reveal that with this combination it is not possible to draw any unambiguous conclusions regarding the mechanism of the ketonization reaction. On the other hand the adsorption coefficient of acetic acid with respect to methanol is more than 3 and one can see from the results plotted in Fig. 2 that the ketonization reaction responds unambiguously to a Langmuir-Hinshelwood model. Thus one can conclude that the surface reaction of acetic acid on iron oxide follows a Langmuir-Hinshelwood mechanism.

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Kinetic Isotope Effect in Chromic Acid Oxidation of Acetophenone

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The observed kinetic isotope effect (=2·13) in the oxidation of $PhCOCH_3$ and $PhCOCH_2D$ by chromic acid is explained by assuming a primary kinetic isotope effect (=5·0) and secondary kinetic isotope effect (=1·66).

WATERS and coworkers[1] in the oxidation of cyclohexanone by chromic acid have shown that the reaction involves participation of an enol intermediate. Their conclusions are based on the primary kinetic isotope effect $k_H/k_D = 5{\cdot}0$ and the solvent isotope effect $k_{D_2O}/k_{H_2O} = 4\text{-}5$. Participation of the enol intermediate has also been demonstrated by Rocek and Riehl[2] in the chromic acid oxidations of isobutyrophenone and 2-chlorocyclohexanone. We now report in this note our observations on both primary and secondary kinetic isotope effects in the oxidation of acetophenone by chromic acid.

Table 1 — Rate Constants for the Chromic Acid and Oxidation of Acetophenone and Acetophenone-α-*d* at 50°C {$[Cr(VI)]=5{\cdot}5\times10^{-3}M$; $[HClO_4]=4{\cdot}05M$; $[PhCOCH_3]=0{\cdot}102M$; $[PhCOCH_2D]=0{\cdot}093M$; solvent: 50% AcOH (v/v)}

Substrate	$k_1^{*}\times10^5$ sec^{-1}	10^3k_1/[Ketone] litre mole^{-1} sec^{-1}
$PhCOCH_3$	87·72	8·60
$PhCOCH_2D$	37·61	4·04

*Mean of triplicate runs.

The reagents used were either chemically pure or were purified using conventional methods. Deuterated acetophenone (α-*d*) was prepared by the method of Jones *et al.*[3] PMR analysis showed only 33% deuteration suggesting the formation of $C_6H_5COCH_2D$.

Kinetic measurements — The reaction was followed by quenching the aliquots at different time intervals with a slight excess of acidified ferrous ammonium sulfate (AR grade) solution and then estimating titrimetrically the ferrous ions, left unreacted against standard $K_2Cr_2O_7$ using barium diphenylamine sulphonate as the indicator.

An apparent primary kinetic isotope effect, $k_H/k_D = 2{\cdot}13$, was calculated from the data given in Table 1. In the case of acetophenone there will be an statistical effect in the sense that removal of the three hydrogen atoms of $-CH_3$ group is equally possible. However, in the case of deuterated analogue the rate would include the possibility of removal of H as well as D from $-CH_2D$ group. But the probability of removal of H is twice that of D. Further because of the presence of C-D bond, the rate at which C-H fission would take place in the deuterated sample will be less than that for C-H fission in acetophenone (secondary kinetic isotope effect k_H/k_H^{1}). The rate of oxidation of dueterated acetophenone would, therefore, be equal to $2k_H^{1}+k_D$, as shown below:

$$\begin{tikzcd}
PhCOCH_3 \arrow[r, "3k_H"] & PhCOCH_2OH \\
PhCOCH_2D \arrow[ur, "k_D"] \arrow[r, "2k_H^{1}"'] & PhCOCHD(OH)
\end{tikzcd}$$

In the case of chromic acid oxidation of cyclohexanone, Waters and coworkers[1] have reported the value of primary kinetic isotope effect k_H/k_D to be equal to 4-5. Assuming $k_H/k_D = 5$ in the present case also, one can calculate the secondary kinetic isotope effect $k_H/k_H^{1} = 1{\cdot}66$ from the relation:

$$3k_H/(2k_H^{1}+k_D) = 8{\cdot}6/4{\cdot}04 = 2{\cdot}13$$

A secondary kinetic isotope effect of this magnitude has also been reported by Bell[4]. Thus the observed rate of chromic acid oxidation of $PhCOCH_2D$

could be explained assuming a primary kinetic isotope effect, $k_H/k_D = 5{\cdot}0$, and a secondary kinetic isotope effect, $k_H/k_H^1 = 1{\cdot}66$.

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Xanthates of Bis(cyclopentadienyl)Ti(IV)

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Xanthate derivatives of bis(cyclopentadienyl) Ti(IV) have been prepared as orange red compounds by reacting potassium alkyl xanthates, R-OCS$_2$K (R = Me, Et, *n*-Pr, *n*-Bu or *n*-Amyl) with bis(cyclopentadienyl) Ti(IV) dichloride in aqueous medium. The complexes are suggested to be of the form (Cp)$_2$Ti(Axan)$_2$, (Axan = alkyl xanthate) on the basis of their colour, metal analysis, and infrared spectral data. Conductance measurements in the case of (Cp)$_2$Ti(MeXan)$_2$ show it to be non-electrolyte supporting the above formulation for the compounds. The compounds have poor solubilities in the common organic solvents, and are unstable in air.

COUTTS *et al.*[1] have reported the preparation of xanthates of Ti(III) by reacting stoichiometric quantities of bis(cyclopentadienyl) Ti(III) chloride with sodium salts of alkyl xanthates. In these compounds xanthate groups are supposed to behave as bidentate ligands similar to the corresponding dithiocarbamates[2-4]. There is, however, no report so far on the preparation of Ti(IV) xanthates.

During the course of our investigations it was found that freshly prepared, saturated aqueous solution of bis(cyclopentadienyl) Ti(IV) dichloride, (Cp)$_2$TCl$_2$, reacted instantaneously with potassium alkyl xanthates, R-OCS$_2$K (R = Me, Et, *n*-Pr, *n*-Bu, *n*-Amyl) to give orange red compounds. The colour intensity of the compounds increased with increasing hydrocarbon chain length of the xanthate part. These compounds may be of the form (Cp)$_2$Ti Axan)$_2$ (Axan = alkyl xanthate) as shown by their colour, metal analysis and IR data. These compounds are sensitive to air and decompose on keeping. Attempts to prepare these compounds by reacting (Cp)$_2$TiCl$_2$ with potassium alkyl xanthates in solvents like THF and acetone resulted in the formation of only the decomposed products. While the reaction appears to be quite complicated, it would appear that (Cp)$_2$Ti^{2+} species is involved in the reactions with the other ligands. The reaction may therefore be written as: (Cp)$_2$Ti^{2+} + 2ROCS$_2^-$ = (Cp)$_2$Ti(ROCS$_2$)$_2$ where R = Me, Et, *n*-Pr, *n*-Br or *n*-Amyl.

TABLE 1 — METAL ANALYSIS AND MELTING POINT DATA OF THE COMPOUNDS

Compounds (Cp)$_2$Ti(Axan)$_2$	m.p. (°C)	Ti (%)	
		Found	Calc.
A = Me	169	11·44	12·27
A = Et	158	11·63	11·43
A = *n*-Pr	156	10·86	10·71
A = *n*-Bu	153-4	10·64	10·09
A = *n*-Amyl	150	9·78	9·52

None of these compounds was found to contain chlorine as tested by the usual qualitative tests. The rate of decomposition appears to increase with decrease in the hydrocarbon chain length of the xanthate part. The compounds are insoluble in water and ethyl alcohol, but sparingly soluble in acetone, benzene, chloroform, carbon tetrachloride, dichloromethane, diethyl ether and nitrobenzene. On keeping, the compounds undergo fast decomposition, apparently losing the CS$_2$ moiety. The molecular weight measurements and NMR studies could not be carried out due to very low solubility of the compounds in the usual solvents.

The molar conductance of a $10^{-3}M$ solution of (Cp)$_2$Ti(Me-Xan)$_2$ in nitrobenzene was found to be 0·3 ohm^{-1} cm^2 mole^{-1} indicating that the compounds is non-electrolyte.

Xanthates are known to have four characteristic bands in the IR region. Bands occurring around 1250 ± 10; 1110 ± 10; 1040 ± 10 cm^{-1} in the present compounds have been assigned to ν(C = S), ν(C—S), ν(C—O) and ν(R—O) vibrations which are highly coupled. The band assignments for (Cp)$_2$Ti(Axan)$_2$ have been made on the basis of those reported for [(Cp)$_2$V(Xan)] complex ion[5]. The band expected around 550 cm^{-1} is not present in the present compounds but may correspond to a broad absorption around 510 cm^{-1} in the spectra of some of the compounds. The bands arising from two cyclopentadienyl groups occur consistently at 3100, 1430, 1010 and 800-815 cm^{-1} in all the compounds suggesting the presence of π-bonded cyclopentadienyl groups.

IR spectra of the compounds were recorded (KBr) on a Perkin-Elmer spectrophotometer model 621. Conductance measurements of the compounds were carried out on a Beckmann conductivity bridge (model RC-18A). Titanium was estimated as TiO$_2$ gravimetrically (Table 1).

Bis(cyclopentadienyl)Ti(IV) dichloride was prepared by the reaction of (cyclopentadienyl) sodium with TiCl$_4$ in THF[6]. Its freshly prepared aqueous solutions[7] were used for preparing the xanthate compounds.

Potassium alkyl xanthates were prepared by the literature methods[8].

Bis(alkyl xanthate)bis(cyclopentadienyl)Ti(IV): A concentrated aqueous solution of potassium alkyl

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