

## THE OXIDATIVE DEHYDROGENATION OF SECONDARY ALCOHOLS CATALYZED BY IRIIDIUM

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The paper deals with the reaction of four secondary alcohols  $RCHOHCH_3$ , where  $R = CH_3$ ,  $C_2H_5$ ,  $i-C_3H_7$  and  $t-C_4H_9$ , with oxygen in gaseous phase on an Ir/C catalyst at 130–160°C. These conditions have proved highly selective for the formation of ketones. The kinetics of the reaction, the kinetic isotope effects of deuterium and the effect of structure of the alcohol on reactivity have been investigated. The reaction rate can be described by an exponential equation or a redox type equation. The rate-controlling step is the splitting-off of hydrogen from the  $\alpha$ -carbon, whereas the release of hydrogen from the hydroxyl group is very rapid. Of the structural effects the steric effect appears to be the most important one.

The reaction of alcohols with oxygen, catalyzed by the platinum group metals, has thus far been regarded as a deep oxidation, especially if conducted in the gaseous phase<sup>1,2</sup>. Zdražil and Kraus<sup>3</sup> have recently shown that rhodium, ruthenium and iridium can be employed as selective catalysts for the conversion of secondary alcohols into ketones by oxidative dehydrogenation under mild conditions (reaction (A)). This paper describes a more detailed study of the course of this reaction in gaseous phase on an iridium catalyst. The problems of the reaction mechanism are discussed.



### EXPERIMENTAL

*Chemicals.* The starting alcohols were commercial products of the firms Lachema, Koch-Light and Fluka. They were redistilled over a short column and checked for purity by gas chromatography. The ketones employed as standards for gas chromatography were also commercial products, redistilled before use. The deuterated 2-propanol ( $CH_3CHODCH_3$ ,  $CD_3CDODCD_3$ ) were supplied by the firm Berlin-Chemie, and  $CH_3CDODCH_3$  was obtained by reduction of acetone with deuterium on a platinum catalyst. Hydrogen (for reduction of the catalyst), air and nitrogen, in pressure bottles, were freed from traces of  $CO_2$  and  $H_2O$  by being passed through beds of NaOH, silica gel and a molecular sieve. The catalyst was prepared by impregnating active

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carbon (Supersorbon), grain size 0.25 to 0.4 mm, with a 0.6% solution of ammonium hexachloro-iridate(IV); the mixture was left standing for 24 h, then the carbon with the adsorbed salt was separated and dried at 100°C. Every weighed portion of the catalyst was reduced directly in the reactor by a mixture of hydrogen and nitrogen (1 : 5) for 30 min and by pure hydrogen for 120 min at 150°C. Depending on the ratio of the active carbon to the solution of the salt the weight contents of iridium in the catalysts were 0.5, 2 and 5%.

*Apparatus.* An all-glass flow apparatus was employed. The catalyst was placed in a tube submerged in a silicone oil bath, kept automatically at a chosen temperature. The variation of temperature within the bed, measured with a thermocouple placed in a well held in the centre of the tube, was  $\pm 1^\circ\text{C}$ . The inner diameter of the bed was 10 mm, the outer diameter of the well was 6 mm. The catalyst was diluted with glass beads of a uniform size. The weights of the catalyst were 10 to 500 mg.

*Procedure.* The bed of the reduced catalyst was flushed with nitrogen and brought to the temperature desired, whereupon air, nitrogen and finally an alcohol were introduced at chosen rates. The first sample of the liquid product, condensed at  $-78^\circ\text{C}$ , was withdrawn after 15 min, next samples were taken at 10-min intervals. Their compositions were determined by gas chromatography on 15% diglycerol on Chromosorb at  $90^\circ\text{C}$ , in an apparatus Chrom 2 with flame-ionization detection. The quantitation was based on the heights of the peaks that had been obtained by calibration. In some experiments we also determined gravimetrically the formed  $\text{CO}_2$ , adsorbed on Ascarite. Since the catalyst exhibited a constant activity, a single weighed portion of the catalyst was used for determining the conversions under different conditions. However, there were differences in activity due to bad reproducibility of the reduction. For this reason each weighed portion of the catalyst was tested on 2-butanol under standard conditions and the conversions were normalized for a common, standard activity<sup>4</sup>.

*Kinetic measurements.* To determine the kinetics the apparatus was operated as a pseudo-differential flow reactor. The corrected conversions  $x$  (up to 12%), obtained at given temperature and partial pressures of the reactants  $p_A$ ,  $p_O$  and different space velocities ( $F_A/W$ ), were used to determine the initial reaction rates from the plots of  $x$  vs  $W/F_A$ . The slopes of the straight lines represent the initial reaction rates,  $r$ . The obtained values of the triplet  $r - p_A - p_O$  for different temperatures served us in selecting a suitable rate equation. Employing the methods of the linear and the non-linear regressions<sup>5</sup> we investigated how the individual triplets for the respective temperatures and each alcohol fitted the assumed rate equations. Since the exponential equation (1) and the Langmuir-Hinshelwood equations had three constants, whereas most of the redox type equations contained only two, we first singled out the best-fitting equations for every group with the aid of the sums of the squared deviations of the calculated and the determined reaction rates. The criterion for further selection from these equations was the temperature dependence for 2-butanol.

*The kinetic isotope effects.* Their values were determined on the basis of experiments with normal 2-propanol and with the deuterated propanols at  $160^\circ\text{C}$  and partial pressures of the alcohol and oxygen of 0.2 and 0.08 atm, respectively. A series of experiments was performed with each alcohol; the conversions were 4 to 20%, depending on the space velocity. The values of the isotope effect were calculated from the conversion ratio  $\alpha = x_H/x_D$ .

## RESULTS AND DISCUSSION

In the first series of experiments we investigated the selectivity of oxidative dehydrogenation on the iridium catalyst. At  $160^\circ\text{C}$ , partial pressures of 2-butanol  $p_A = 0.05$

atm and oxygen  $p_{\text{O}} = 0.1$  atm (nitrogen made up the pressure to 1 atm) the conversions of the alcohol were determined for different space velocities, and the conversions to the ketone and to carbon dioxide were calculated. Fig. 1 shows that the total oxidation was not significant and was probably a parallel reaction. In the kinetic measurements the conversions of the alcohols were low, so that the role of the total oxidation could be neglected. The purpose of the next series of experiments was to investigate the effect of concentration of the metal in the catalyst on its activity. From the data in Table I it follows that the conversion depended on the amount of the metal in the reactor, but not on its amount in a weight unit of the catalyst. In further experiments the catalyst employed contained 0.5% of Ir (w/w). The plots of the initial reaction rates *vs* the ratio of the constituents at different dilutions with nitrogen are shown in Fig. 2. From this survey it is seen that reactivity decreased in the order 2-propanol, 2-butanol, 3-methyl-2-butanol and 3,3-dimethyl-2-butanol. The data taken from Fig. 2 were processed by means of various kinetic equations, in an attempt to pick out the best-fitting one. The set of equations that were selected first consisted of the exponential equation (1), 20 Langmuir-Hinshelwood equations

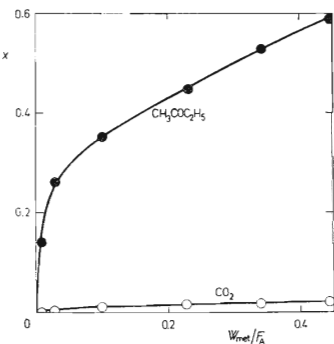


FIG. 1

Conversion ( $x$ ) of 2-Butanol to 2-Butanone and to Carbon Dioxide at  $160^{\circ}\text{C}$  and a Two-fold Stoichiometric Amount of Oxygen in Relation to the Reciprocal Value of the Space Velocity  $W_{\text{met}}/F_A$  ((g of iridium).h/mol of alcohol).

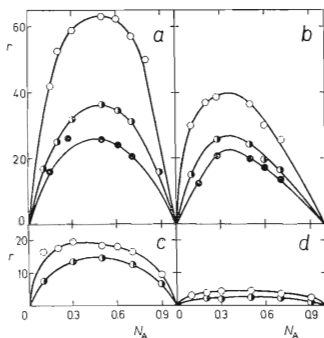


FIG. 2

The Initial Rates of Oxidation of Alcohols to Ketones at  $150^{\circ}\text{C}$  in Relation to the Ratio of the Reactants

*a* 2-Propanol, *b* 2-butanol, *c* 3-methyl-2-butanol, *d* 3,3-dimethyl-2-butanol,  $\circ$   $p_A + p_{\text{O}} = 0.2$  atm,  $\bullet$   $p_A + p_{\text{O}} = 0.1$  atm,  $\ominus$   $p_A + p_{\text{O}} = 0.07$  atm,  $N_A = p_A/(p_A + p_{\text{O}})$ .

TABLE I

The Effect of the Content of Metal on the Conversion of 2-Butanol to 2-Butanone

Reciprocal space velocity  $W_{\text{met}}/F_A = 7600 \text{ g h/mol}$ ,  $160^\circ\text{C}$ , partial pressure of the alcohol  $p_A = 0.20 \text{ atm}$ .

$\text{Ir/C}$ %	$W_{\text{cat}}$ g	$W_{\text{met}}$ mg	Conversion at $p_0$ , atm		
			0.04	0.08	0.12
0.5	0.1	} 5 {	0.098	0.150	0.184
2.0	0.025		0.100	0.134	0.170
5.0	0.01		0.100	0.146	0.184

TABLE II

Values of the Constants of Equation (J) for  $150^\circ\text{C}$ 

Constant	2-Propanol <sup>a</sup>	2-Butanol <sup>a</sup>	3-Methyl-2-butanol	3,3-Dimethyl-2-butanol
$k'$ <sup>b</sup>	614	184	110	27
$a$	0.49	0.25	0.30	0.34
$b$	0.49	0.47	0.45	0.48

<sup>a</sup>  $130^\circ\text{C}$   $k' = 81$ ,  $a = 0.22$ ,  $b = 0.44$ ;  $160^\circ\text{C}$ ,  $k' = 719$ ,  $a = 0.35$ ,  $b = 0.80$ . Activation energy  $25 \text{ kcal/mol}$ . <sup>b</sup> In units  $[\text{mol/h g atm}^{a+b}]$ .

TABLE III

Values of the Constants of Equation (5) for  $150^\circ\text{C}$ 

Alcohol	2-Propanol	2-Butanol <sup>a</sup>	3-Methyl-2-butanol	3,3-Dimethyl-2-butanol
$k_1$ <sup>b</sup>	2 150	2 968	1 405	228
$k_2$ <sup>c</sup>	267	263	72	15

<sup>a</sup> Activation energy  $E_1 = 15 \text{ kcal/mol}$ ,  $E_2 = 9 \text{ kcal/mol}$ . <sup>b</sup> In units  $[\text{mol/h g atm}]$ . <sup>c</sup> In units  $[\text{mol/h g atm}^{0.5}]$ .

for bimolecular reactions<sup>5</sup> and 10 equations of the so-called redox model<sup>1,6,7</sup>. Out of these, the exponential equation, (1), three Langmuir-Hinshelwood equations, (2) to (4) and one equation of the redox model, (5), proved equally fitting for the data measured at 150°C.

$$r = k' p_A^a p_O^b, \quad (1)$$

$$r = k K_A K_O p_A p_O / [1 + K_A p_A + (K_O p_O)^{0.5}]^4, \quad (2)$$

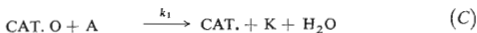
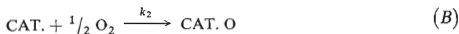
$$r = k K_A K_O p_A p_O / [1 + (K_A p_A)^{0.5} + K_O p_O]^4, \quad (3)$$

$$r = k K_A K_O p_A p_O / [1 + (K_A p_A)^{0.5} + (K_O p_O)^{0.5}]^4, \quad (4)$$

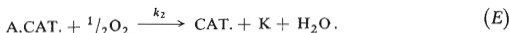
$$r = k_1 k_2 p_A p_O^{0.5} / (1/2 k_1 p_A + k_2 p_O^{0.5}). \quad (5)$$

Further selection from these was based on measuring the kinetics of oxidative hydrogenation of 2-butanol at 130 and 160°C. The results eliminated equations (2) to (4); these gave bad correlation, or their constants did not fit either the Arrhenius or the van't Hoff equation. The values obtained for equation (1) are listed in Table II. However, this equation has an empirical character and is not suitable for considerations of the reaction mechanism. For this reason we analyzed equation (5) only; the values of its constants are given in Table III.

Equation (5) can be derived from two model conceptions. According to one of these, analogous to the oxidation schemes on oxide catalysts<sup>6,7</sup>, the first step (B) is a reaction of oxygen in the gaseous phase with the catalyst and the oxide formed on the surface reacts in the second step (C) with the gaseous alcohol.



According to the other model the first step is adsorption of the alcohol, which is then attacked by oxygen:



In either case the two steps are assumed to have comparable rates in steady state and in either case equation (5) is obtained.

According to reactions (B) and (C) the rate constant  $k_2$  should be independent of the structure of the substrate. However, Fig. 1 and Tables II and III show that this was not the case. By contrast, the scheme of reactions (D) and (E) concedes that the two rate constants may depend on the structure of the reacting alcohol. Therefore, this scheme appears more probable. As will be shown below, however, the simplicity of the scheme makes it impossible to account for other experimental findings.

The structural dependences of the rate constants in Tables II and III are correlable with the Taft equation<sup>8</sup>. The logarithms of the constant  $k$  in equation (1) give a good correlation against the substitution constants  $\sigma^*$  for R in  $\text{RCHOHCH}_3$ , the slope  $\sigma^*$  being 4.7. On the other hand, the logarithms of the constants  $k_1$  and  $k_2$  in equation (5) are better consistent with the steric constants  $E_s$ , both having a common slope  $s = 0.7$ . However, the number of data is so small that it is hardly possible to judge which of the two correlations is the more appropriate one.

A more substantial information has been obtained by measuring the kinetic isotope effects. Their calculation from the conversion of the non-deuterated and the deuterated alcohol requires approximations (in order to be consistent with the ratio of the rate constants) since the kinetics are rather complex. However, the values obtained are great enough to make the effect of replacement of hydrogen by deuterium quite evident. For  $\text{CH}_3\text{CDODCH}_3$   $\alpha = 3.7 \pm 0.9$  (average from 6 experiments), for  $\text{CD}_3\text{CDODCD}_3$   $\alpha = 3.2 \pm 0.1$  (average from 3 experiments) and for  $\text{CH}_3\text{CHODCH}_3$   $\alpha = 1.0 \pm 0.1$  (average from 4 experiments). The maximum isotope effect calculated<sup>9</sup> from the stretching vibrations of the bonds  $\text{C}_\alpha\text{—H}$  and  $\text{C}_\alpha\text{—D}$  in alcohols was  $\alpha_{\text{max}} 3.8$ . This data suggest that cleavage of the  $\text{C}_\alpha\text{—H}$  bond is the rate-controlling step and that the  $\text{O—H}$  bond is split very promptly. The same findings were reported<sup>10,11</sup> on the oxidation of deuterated 2-propanols in liquid phase by various agents. Hence it seems that the reaction in the gaseous phase and in the liquid phase proceed by similar mechanisms.

Confrontation of the measured kinetic isotope effects with the kinetic model expressed by reactions (D) and (E) reveals discrepancy. The splitting-off of the two hydrogen atoms are two separate steps, whereas the model postulates only one. Consequently, the model should be amended to include abstraction of the hydroxyl hydrogen from the oxygen atom as another and very rapid (and thus probably equilibrium) step. The form in which oxygen reacts is not clear, so that its activation on the catalyst surface should also be a step considered in the model. These amendments, however, would make the reaction scheme so complex that no usable rate equations could be derived; only after the introduction of simplifying assumptions would the equations become formally similar to equation (5). Thus equations (D) and (E) can therefore be regarded as the nucleus of a more complex reaction scheme.

Correlation of the rate constants of different alcohols with Taft's induction and steric constants has not allowed us to decide, with the aid of statistical criteria,

which effect is the dominating one. A positive value of the reaction parameter  $\rho^*$ , correlated with the induction constants  $\sigma^{\ddagger}$ , would have to be interpreted as facilitation of the reaction by reducing the electron density on  $C_{\alpha}$ , *i.e.* as a nucleophilic attack of the adsorbed oxygen atom or molecule on this carbon. An alternative explanation of the observed effect of substituents on the reaction rate, based on correlation with the steric constants, is a decrease in reaction rate with the increasing steric hindrance. Since this hindrance is known to be the predominant effect in heterogeneously catalysed reactions we tend to prefer the latter interpretation.

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