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Linear Free Energy Relationships in Heterogeneous Catalysis

XI. Deep Oxidation of Lower Olefins on Nickel Oxide Catalyst

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Linear free energy relationship studies were made on the rates of deep oxidation of some lower olefins over a nickel oxide catalyst. Since the trend of reactivities of olefins seems to be determined by the type of allylic hydrogens and their number for each olefin, quite similar treatments as previously reported on the dehydrogenation of cyclohexanes may be applied to this case. That is, the overall rate of deep oxidation of olefin R at temperature T, $v(\mathrm{R},T)$, can be represented as the weighted sum of the characteristic rates for allylic hydrogen atoms as

$$v(\mathrm{R},T) = \sum_m w(\mathrm{R},m) \cdot v(m,T)$$

where $w(\mathrm{R},m)$ means the statistical factor, i.e., the number of mth allylic hydrogen (primary, secondary, or tertiary) for olefin R and $v(m,T)$, the rate of the mth hydrogen at temperature T. The logarithm of $v(m,T)$ is demonstrated to have a linear relationship with delocalizability, $D_r^{\mathrm{R}}(H)$, a quantum chemical reactivity index for hydrogen abstraction, as

$$\log v(m,T) = \log v(0,T) + \gamma(T) \cdot \Delta D_r^{\mathrm{R}}(\mathrm{H}^m)/2.3RT$$

where $v(0,T)$ is the rate of hypothetical hydrogen with delocalizability of 1.00 and $\gamma(T)$ is a proportional constant. Furthermore, $\gamma(T)$ is proved to be practically independent of temperature. This means that the preexponential factor of the mth hydrogen, $v(m,\infty)$, is independent of the type of allylic hydrogen but its activation energy, $E_{\mathrm{A}}(m)$, decreases proportionately with $D_r^{\mathrm{R}}(\mathrm{H}^m)$. Finally, the overall rates can be expressed as follows:

$$v(\mathrm{R},T) = \sum_m w(\mathrm{R},m) \cdot v(0,\infty) \cdot \exp\{-[E_{\mathrm{A}}(0) - \gamma^{\mathrm{D}} \cdot \Delta D_r^{\mathrm{R}}(\mathrm{H}^m)]/\mathrm{R}T\}$$

where $v(0,\infty)$ and $E_{\mathrm{A}}(0)$ are the preexponential factor and the activation energy, respectively, for hypothetical hydrogen defined above and $\gamma(T)$ is rewritten as γ^{D}. Finally, the rate of deep oxidation of any olefin at any temperature can be predicted according to the above equation using the delocalizability inherent to allylic hydrogen and three parameters characteristic of the type of catalyst, i.e., $v(0,\infty)$, $E_{\mathrm{A}}(0)$ and γ^{D}. This treatment is compatible with the tentative mechanism that the deep oxidation of olefins over nickel oxide involves an abstraction of allylic hydrogen as a rate determining step.

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INTRODUCTION

For the interpretation of heterogeneous catalysis, it is desirable to obtain quantitative relationships between the reaction rates of a series of reactants and their reactivity parameters. From the standpoint of general application, such parameters should be the calculable ones, e.g., thermodynamic or quantum-chemical. Recently, several authors have established that the oxidation of propylene on bismuth molybdate or cuprous oxide catalysts proceeds through initial abstraction of an allylic hydrogen (*1*), and that its rate-determining step is the formation of the allyl intermediate as in the case over bismuth molybdate (*2*). By extensive research on the oxidation of several lower olefins over bismuth molybdate catalyst, Adams *et al.* (*3*) have indicated that their reactivities are parallel to those of allyl hydrogen abstraction by free radicals. Then, the oxidation of these lower olefins may also follow the same allyl mechanism as of propylene over these catalysts. In the present investigation, the aim has been to provide a more general reactivity parameter for oxidation of lower olefins and to apply it to their deep oxidation over nickel oxide catalyst.

EXPERIMENTAL

All the reactant gases used are tabulated in Table 1. Ethylene was supplied from the Nippon Petroleum Co., Ltd.; propylene from the Chisso Chemicals Co. Ltd.; butenes from the Phillips Co. Ltd.; 1-pentene, 3-methyl-1-butene, and 2-methyl-2-butene from the Tokyo Kasei Co. Ltd. The purity of these reactants is above 99% except for 2-methyl-2-butene, whose purity is above 95%. The olefins were purified by a cycle of vaporization and condensation with liquid nitrogen to eliminate permanent gases and condensable impurities, if any.

The oxidation rates of olefins were measured by a microcatalytic technique, which is suitable for the rapid and exact measurements of the rates of a homologous series of reactants on a relatively fresh catalyst surface. The fully automatic system previously developed by us was used (*4*). With this apparatus, it was possible to make a series of automatic measurements where the reaction conditions, i.e., the reactant gases, their partial pressures and/or the reaction temperatures, were successively changed in any sequences as desired.

Sample gases, 3.0% olefin in pure oxygen, were prepared by premixing the gases and allowing them to stand for two or three days. This feed gas was compressed into a sample inlet stopcock (15 ml) to exactly the same pressure as that of the carrier stream, then introduced into the carrier gas as a pulse by a pneumatic displacement of the stopcock. The pulse was then carried to a reactor consisting of a glass tube (16 mm o.d.) equipped with a sintered glass disc for supporting catalyst and a thin sheath for a thermocouple. All of the unchanged reactants and the product carbon dioxide were analyzed gas chromatographically, using a 70 cm column packed with silica gel (32–60 mesh) for ethylene, or a 2 m one with diisodecylphthalate for other olefins. The latter column was used at room temperature, except for propylene where it was cooled to about 0°C. Water as another reaction product could not be analyzed with these columns because of too large a retention volume. Oxygen was used as a carrier gas in order to keep the catalyst always in the oxidized state and to obtain the relative reaction rates in the presence of a large excess of oxygen. The cell current was kept as low as 50 mA. In order to restore the decrease in the sensitivity due to the above procedures, the signal output was amplified electronically up to ten times. The catalyst weight (0.1–0.9 g) was selected so that the conversion did not exceed 20%. The catalysts were diluted with 1 g of silicon carbide (30–60 mesh). The reaction was carried out between 180 and 250°C, controlled within ±1°C. The catalyst used was the nickel oxide, Ni-2-700-8 (*5*), prepared by the calcination of nickel carbonate at 700°C for 8 hr.

TABLE 1

KINETIC DATA AND SOME MOLECULAR PARAMETERS OF VARIOUS OLEFINS

olefin	v (ml min^{-1} g^{-1}) at 215°C	E_A(R) (kcal/mole)		m	w(R,m)	D_r^R(H)
		obsd	calcd			
ethylene	1.26	13.0	—	—	—	—
propylene	4.27	16.9	16.6	1	3	1.0048
cis-2-butene	6.46	16.4	16.6	1	6	1.0050
trans-2-butene	7.40	16.5	16.6	1	6	1.0050
isobutene	6.18	17.3	16.6	1	6	1.0063
2-methyl-2-butene	11.37	16.4	16.6	1	3	1.0051
					6	1.0065
1-butene	7.30	15.7	15.7	2	2	1.0169
1-pentene	8.64	15.3	15.7	2	2	1.0179
2-pentene	10.61	15.9	16.0	1	3	1.0050
				2	2	1.0171
3-methyl-1-butene	9.70	14.5	14.6	3	1	1.0302
4-methyl-2-pentene	11.92	15.2	15.2	1	3	1.0050
				3	1	1.0302

RESULTS AND DISCUSSION

The oxidation of lower olefins on the nickel oxide catalysts was found to give only carbon dioxide as a carbon-containing product in each pulse, but some of the olefin introduced was held irreversibly on the catalyst. For example, in the oxidation of 1-butene at 250°C in an oxygen and nitrogen mixture, 2.5 mole % of the reactant was converted to carbon dioxide and 90.5 mole % was recovered unchanged; thus 7.0 mole % was lacking. When this catalyst was treated in the above mixture stream immediately after the reaction, with the temperature being allowed to rise gradually up to 400°C over about 3 hr, and the desorption products were trapped with liquid nitrogen, 2.3 and 4.3 mole % of the 1-butene introduced were found to be recovered as intact butenes and carbon dioxide, respectively. The total amount of these desorption products nearly agrees with that of the 1-butene lost. On the introduction of only the carbon dioxide as a pulse, it passed through the catalyst bed without any irreversible adsorption. Almost the same results as above were obtained on other olefins as well.

Therefore, it may be concluded that a fraction of the olefin, introduced as a pulse, is held irreversibly on the catalyst surface as a strongly adsorbed olefin but not as the carbon dioxide produced. Furthermore, the reactivities of the irreversibly adsorbed olefins are believed to be very small. Belousov *et al.* (*6*) have also proposed the same idea as above, on the basis of their extensive research on the oxidation of propylene by a pulse technique over many kinds of oxides. Consequently, the amount of carbon dioxide that was produced promptly in a pulse was always used to evaluate the reactivities of a series of olefins in the present investigation.

Reproducible results were always obtained when the catalysts were pretreated with sufficient oxygen at 300°C for 2 hr and furthermore subjected to oxygen treatment at 300°C for 20 min after each pulse. Since the apparent order in propylene was found to be nearly zero below 30% of conversion, the reaction rate was expressed as a product of the conversion to carbon dioxide and F/W, where F is the flow rate of the carrier gas and W the catalyst weight. The reaction rate at each condition was obtained as the average value from two or three runs. Arrhenius plots of some olefins are shown in Fig. 1. The reaction rates and the activation energies of all the olefins used are summarized in Table 1.

Generally, olefin molecules have two

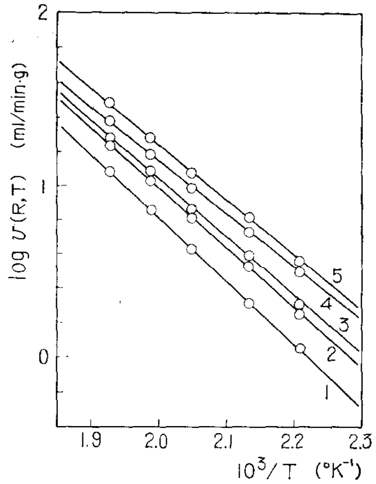

FIG. 1. Arrhenius plots for deep oxidation of some olefins over nickel oxide. 1, propylene; 2, *t*-2-butene; 3, 1-butene; 4, 3-methyl-1-butene; 5, 4-methyl-2-pentene.

kinds of reactive points; the one is a double bond and the other an allylic hydrogen. In the oxidation of olefins with atomic oxygen or peracids, the reaction is shown to proceed via addition of oxygen to a double bond. The catalytic oxidation of olefins on bismuth molybdate or cuprous oxide catalysts has been confirmed to involve a hydrogen abstraction from an allylic position (*1–3*).

The results shown in Fig. 1 and Table 1 indicate that the reactivities in the deep oxidation of olefins seem to be determined by the type of allylic hydrogen and their number; the reactivity, except for ethylene, tends to increase and the activation energy to decrease in the order of primary, secondary, and tertiary allylic hydrogen. These trends cannot be interpreted in terms of the reaction parameter for the addition to the double bond, and are compatible with the tentative mechanism that the deep oxidation of olefins on nickel oxide involves also an abstraction of allylic hydrogen. The only exception is ethylene, which has no allylic hydrogen. Table 1 shows that the reaction rate of ethylene is much smaller than for the other olefins, but the value of the activation energy is unexpectedly small. This may be due to the fact that the oxidation of ethylene may follow a mechanism different from that of other olefins. Therefore, ethylene is excluded from the following analysis.

As in the previous report (*7*) on the dehydrogenation of cyclohexanes, the overall rate of deep oxidation of olefin R at temperature T, $v(\mathrm{R},T)$, may be expressed as the weighted sum of the characteristic rates of hydrogen atoms according to the following equation:

$$v(\mathrm{R},T) = \sum_m w(\mathrm{R},m) \cdot v(m,T). \qquad (1)$$

Here, $w(\mathrm{R},m)$ is the statistical factor, i.e., the number of mth allylic hydrogen (primary, secondary, or tertiary) for olefin R and $v(m,T)$ is the rate for the mth hydrogen at temperature T (°K). Table 1 also shows the value of $w(\mathrm{R},m)$ for each olefin. Since Eq. 1 holds for the ten kinds of olefins used, the three unknown values $v(1,T)$, $v(2,T)$, and $v(3,T)$ are easily calculable by the method of least squares.

In the previous report (*7*) on the dehydrogenation of cyclohexanes, delocalizability, a quantum chemical reactivity index, proved to be useful for the expression of the reaction rate in terms of linear free energy relationships. From the trends of the reactivities for the deep oxidation of lower olefins, possibly involving a homolytic hydrogen abstraction, we infer that the delocalizability is useful for the explanation of the rate of this reaction, too. Thus the delocalizability, $D_r^{\mathrm{R}}(\mathrm{H})$, of each hydrogen in these olefins was computed as in the previous manner (*7*). These values are summarized in Table 1.

Excellent linear relationships between the logarithm of the calculated rate, $v(m,T)$, of each hydrogen and its delocalizability, $D_r^{\mathrm{D}}(\mathrm{H})$, are obtained as is shown in Fig. 2. From these relationships, the following equation holds at each temperature:

$$\log v(m,T) = \{[\gamma(T) \cdot \Delta D_r^{\mathrm{R}}(\mathrm{H}^m)]/2.3RT\} + \log v(0,T). \qquad (2)$$

Here, $\gamma(T)$ is the proportionality constant, $v(0,T)$ is the rate of a hypothetical hydrogen with delocalizability of 1.00, and

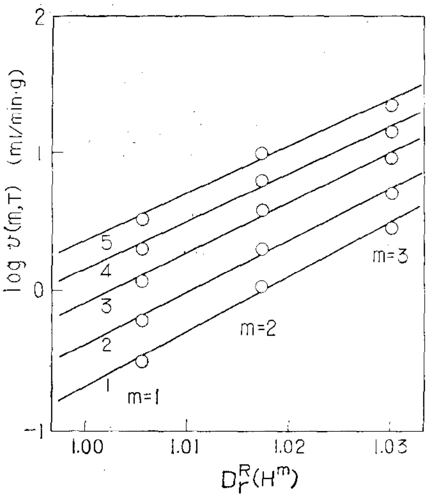

FIG. 2. The relationships between the rate $v(m,T)$ and the delocalizability of the mth allylic hydrogen. 1, 180°C; 2, 196°C; 3, 215°C; 4, 230°C; 5, 246°C.

$\Delta D_r^R(H^m)$ is defined as $(D_r^R(H^m) - 1.00)$.

Arrhenius plots of $v(m,T)$ are shown in Fig. 3; their slopes give the activation energy for the mth hydrogen, $E_A(m)$. $E_A(m)$ is seen to decrease slightly in the order of primary, secondary, and tertiary hydrogen.

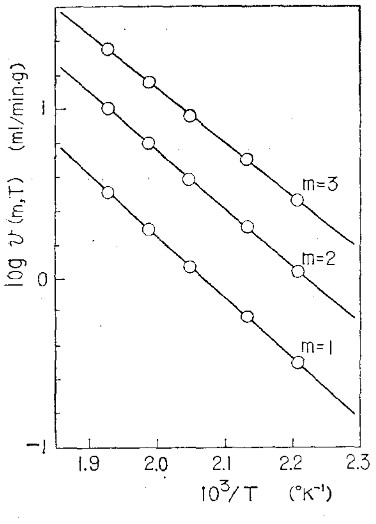

FIG. 3. Arrhenius plots of $v(m,T)$ for each mth allylic hydrogen.

TABLE 2

CALCULATED VALUES OF $\gamma(T)$ AND $v(0,T)$

T (°C)	$\gamma(T)$ (kcal/mole)	$v(0,T)$ (ml min^{-1} g^{-1})
180	82.8	0.199
196	83.0	0.386
215	82.7	0.775
230	82.6	1.341
246	82.5	2.241

Since Eq. 1 and Eq. 2 are proved to hold, two unknown parameters, $\gamma(T)$ and $v(0,T)$, are calculated from the rate data of ten kinds of olefins by the method of non-linear least squares. The calculated values are tabulated in Table 2. $\gamma(T)$ is practically independent of temperature.

Rewriting $\gamma(T)$ as γ^D, Eq. 2 leads to Eq. 3,

$$\log v(m,T) = \log v(0,\infty) - \{[E_A(0) - \gamma^D \cdot \Delta D_r^R(H^m)]/2.3RT\}. \quad (3)$$

Here, $v(0,\infty)$ and $E_A(0)$ stand for the preexponential factor and activation energy, respectively, for the hypothetical allylic hydrogen. Also,

$$\log v(m,T) = \log v(m,\infty) - [E_A(m)/2.3RT], \quad (4)$$

where $v(m,\infty)$ and $E_A(m)$ have the above meaning for the mth hydrogen. Comparison of Eq. 3 and Eq. 4 leads to the following relations:

$$\log v(m,\infty) = \log v(0,\infty), \quad (5)$$

$$E_A(m) = E_A(0) - [\gamma^D \cdot \Delta D_r^R(H^m)]. \quad (6)$$

These relations show that the activation energy, $E_A(m)$, for the mth hydrogen decreases proportionately with $D_r^R(H^m)$, i.e., it decreases in the order of primary, secondary, and tertiary hydrogen, while the preexponential factor, $v(m,\infty)$, is almost independent of the type of allylic hydrogen. The values of $E_A(m)$, obtained from Fig. 2, are plotted against $D_r^R(H^m)$ in Fig. 4. This shows that Eq. 5 and Eq. 6 are well satisfied.

Then, combining Eq. 1 and Eq. 3, the overall reaction rate of the deep oxidation of an olefin R on this nickel oxide catalyst can be represented as the following equation,

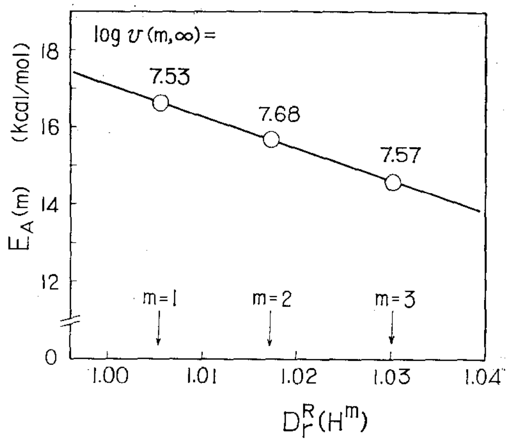

FIG. 4. The relationship between the activation energy and the delocalizability of the mth allylic hydrogen.

$$v(\mathrm{R},T) = \sum_m w(\mathrm{R},m) \cdot v(0,\infty) \cdot \exp\{-[E_A(0) - \gamma^D \cdot \Delta D_r{}^R(\mathrm{H}^m)]/RT\}. \quad (7)$$

On the basis of this equation, the three parameters, $v(0,\infty)$, $E_A(0)$ and γ^D, can be calculated more accurately by the method of nonlinear least squares, since more numerous data (i.e., those of the ten kinds of olefins at the five levels of temperature) are available against only the three unknown parameters as above for analysis of Eq. 7. The results are as follows:

$$\begin{aligned} \log v(0,\infty) &= 7.56 \pm 0.18 \text{ ml min}^{-1}\text{ g}^{-1}, \\ E_A(0) &= 17.1 \pm 0.4 \text{ kcal mole}^{-1}, \\ \gamma^D &= 82.7 \pm 2.3 \text{ kcal mole}^{-1}. \end{aligned}$$

In turn, using these values, the values of $v(\mathrm{R},T)$ are calculated according to Eq. 7 and plotted against their observed values in Fig. 5. A good agreement is obtained between them. However, some deviations may be pointed out in the details of Fig. 5. The calculated values for propylene and 1-pentene are always lower than their observed ones and the reverse is the case for isobutene and 4-methyl-2-pentene. This can be mainly ascribed to an imperfection in the quantum chemical reactivity parameter employed herein; other effects, such as a certain steric effect, may be taken into consideration only after an improvement of this parameter. The activation energy, $E_A(\mathrm{R})$, for each olefin can be represented by the following equation:

$$E_A(\mathrm{R}) = \left[\sum_m w(\mathrm{R},m) \cdot v(m,T) \cdot E_A(m)\right] \Big/ \left[\sum_m w(\mathrm{R},m) \cdot v(m,T)\right]. \quad (8)$$

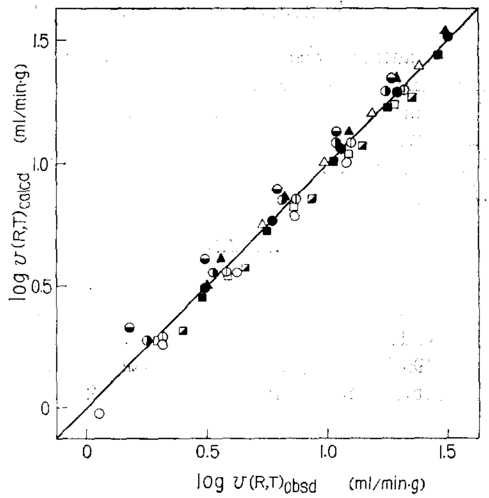

FIG. 5. Comparison of the observed and calculated rates of deep oxidation of olefins over nickel oxide. Reaction temperature: 180, 196, 215, 230, 246°C. ○, propylene; ◐, t-2-butene; ◑, c-2-butene; ⊖, isobutene; ●, 2-Me-2-butene; □, 1-butene; ◩, 1-pentene; ■, 2-pentene; △, 3-methyl-1-butene; ▲, 4-methyl-2-pentene.

The values of $E_A(\mathrm{R})$ were calculated by using the calculated values of $v(m,T)$ at 215°C. Table 1 shows the calculated values of $E_A(\mathrm{R})$ to be in good agreement with the observed ones.

Summarizing the above results, it is concluded that the reactivity of olefins in the oxidation on nickel oxide is determined by the type of allylic hydrogen and the number of them, and the differences in the rates of allylic hydrogens are ascribed to those of the activation energy and not of the preexponential factor. Furthermore, the rates of deep oxidation of lower olefins are satisfactorily expressed on the basis of linear free energy relationships using $D_r{}^R(\mathrm{H})$ as a quantum chemical reaction parameter.

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REFERENCES

1. ADAMS, C. R., JENNINGS, T. J., *J. Catal.* **2,** 63 (1963); SACHTLER, W. M. H., DEBOER, N. H., *Proc. Int. Congr. Catal. 3rd, A* **1,** 252 (1965); VOGE, H. H., WAGNER, C. D., AND STEVENSON, D. P., *J. Catal.* **2,** 58 (1963).
2. ADAMS, C. R., AND JENNINGS, T. J., *J. Catal.* **3,** 549 (1964).
3. ADAMS, C. R., *Proc. Int. Congr. Catal. 3rd, A* p. 240. North Holland, Amsterdam, 1965.
4. UCHIJIMA, T., UEMITSU, N., AND YONEDA, Y., *Kogyo Kagaku Zasshi,* **71,** 1764 (1968).
5. UCHIJIMA, T., TAKAHASHI, M., AND YONEDA, Y., *J. Catal.* **9,** 403 (1967).
6. BELOUSOV, V. M., AND GERSHINGORINA, A. V., *Proc. Int. Congr. Catal. 4th, (Moscow)* (Paper 23 p. 308, 1968). Akadémiai Kiadó, Budapest, 1971.
7. HISHIDA, T., UCHIJIMA, T., AND YONEDA, Y., *J. Catal.* **11,** 71 (1968).