JOURNAL OF CATALYSIS 69, 495–497 (1981)

NOTES

Substituent Effects in the Catalytic Oxidation of Propylene

The use of Hammett theory to correlate electronic effects in reaction mechanisms in heterogeous catalysis has been limited compared to its application in stoichiometric homogeneous systems (*1*). The equation

$$\log(k_X/k_H) = \rho\sigma \qquad (1)$$

correlates the relative reaction rates (k_X/k_H) for a series of compounds of varying electron-donating ($\sigma < 0$) and electron-withdrawing ($\sigma > 0$) properties with the Hammett reaction constant ρ.

This approach has now been applied to the selective oxidation of propylene over bismuth molybdate-based catalysts to probe the nature of the allylic intermediate formed in the rate-determining step (*2*). Rate enhancements observed for aliphatic substituents ($\sigma < 0$) are consistent with, but cannot distinguish between, a radical or a cationic intermediate (*3*). The present work is concerned with the measurement of aromatic substituent effects, since the aromatic nucleus is compatible with both electron-withdrawing and -donating groups.

The relative rates of catalytic oxidation of four allylbenzenes, $pXC_6H_4CH_2CH{=}CH_2$ (X = H, CH_3, OCH_3, Cl) were measured by analysis of the effluent mixture produced from reaction of a 1:1 molar mixture of each of the three substituted: normal allylbenzene pairs at 320°C and 0.5-sec contact time over $Bi_2Mo_3O_{12}$, Bi_2MoO_6, and a multicomponent system ($M_a^{2+}M_b^{3+}Bi_xMo_yO_z$). Under these conditions, the only products detected are the corresponding cinnamaldehyde (the expected oxygen insertion product) and indene.

Based on the reaction scheme for the catalytic oxidation of propylene (*2, 8, 9*), the formation of these two products via a common allylic species, formed in the rate-determining α-hydrogen abstraction step, is the most likely reaction mechanism. Thus, relative reactivities (R_X/R_H) can be calculated from the overall conversions of allylbenzene (AB) and substituted allylbenzene (AB-X) in any pairwise run using the equation

$$\frac{R_X}{R_H} = \frac{k_X K_X}{k_H K_H} = \frac{\log\,[AB/AB_0]}{\log\,[(AB-X)/(AB-X)_0]}. \qquad (2)$$

The use of the homologous series of allylbenzenes substituted in the *para* position minimizes the contribution of the adsorption coefficient terms (K) and thus, relative reactivities mainly reflect chemical rate constants (k).

The relative rates for catalytic oxidation

TABLE 1

Comparison of Relative Rates at 320°C for Catalytic Oxidation of $pXC_6H_4CH_2CH{=}CH_2$ over $Bi_xMo_yO_z$ (Eq. (3)) and Benzyl Radical-Forming Azo Decomposition (Eq. (4))

X	Catalytic oxidation, R_X/R_H[a]	Azo decomposition, k_Xk_H[b]
H	1.00	1.00
CH_3	1.55	1.18
Cl	1.98	2.43
OCH_3	3.03	1.34

[a] Average for Bi_2MoO_6, $Bi_2Mo_3O_{12}$, and $M_a^{2+}M_b^{3+}Bi_xMo_yO_z$ (all values within ±5% of average); 0.5 sec, total olefin conversion = 1.0–2.5%.

[b] Corrected to 320°C for the effect of one X group, assuming 2-bond C–N cleavage in rate-determining step in Eq. (4) (*6*).

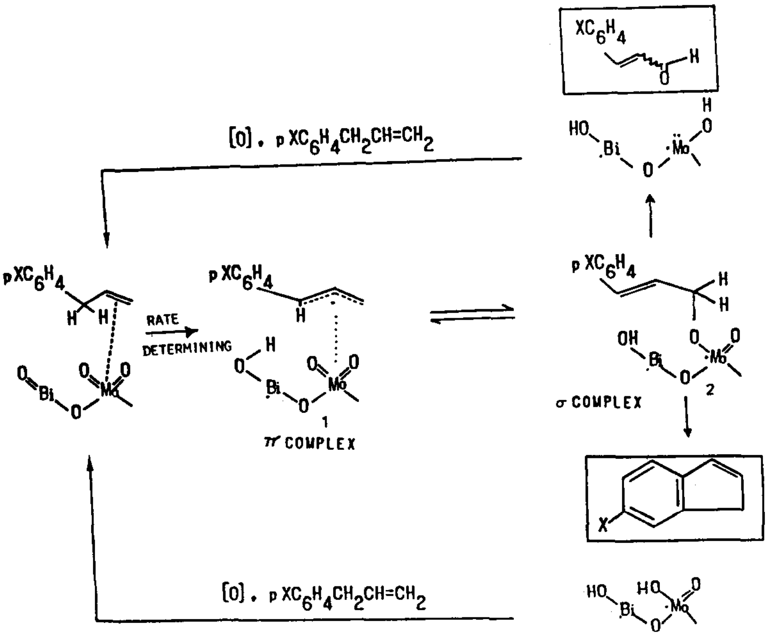
0021-9517/81/060495-03$02.00/0

of $pXC_6H_4CH_2CH{=}CH_2$ over $Bi_2Mo_3O_{12}$, Bi_2MoO_6, and $M_a^{2+}M_b^{3+}Bi_xMo_yO_z$ show the same rate enhancements (within ±5%) for any given group X (Table 1). Both electron-withdrawing and -donating groups exhibit relatively small rate enhancements. These results are indicative of the formation of a radical-like rather than an ionic intermediate in the rate-determining step (*4, 5*). A comparison of the substituent effects for the catalytic oxidation of allylbenzene (Eq. (3)) with those for the benzyl radical-forming nitrogen extrusion from 2-phenylazoethanes (*6*) (Eq. (4)) illustrates that small rate enhancements for both electron-withdrawing and -donating groups are a general feature of both reactions (Table 1). The rate of allylic hydrogen atom abstraction from $pXC_6H_4CH_2CH{=}CH_2$ by *tert*-butoxy radicals also follows the order $X{=}OCH_3 > CH_3 > H_4$ (*7*).

$$p\text{-}XC_6H_4CH_2CH{=}CH_2 \xrightarrow[320°C,-H]{Bi_xMo_yO_z,\ O_2} p\text{-}XC_6H_4CH{=}\dot{C}H{=}CH_2 \qquad (3)$$

$$pXC_6H_4(CH_3)CH{-}N{=}N{-}CH(CH_3)C_6H_4pX \xrightarrow{\Delta,-N_2} 2pXC_6H_4\dot{C}H(CH_3) \qquad (4)$$

An overall mechanism consistent with current results and those of previous studies (*8, 9*) is shown in Scheme 1. Formation of both cinnamaldehyde and indene proceeds via a π-allylic radical-like surface complex **1**, formed in the rate-determining step via α-hydrogen abstraction, which undergoes C–O bond formation to give the common σ-O allyl molybdate intermediate **2**. Indene is formed via heterolytic C–O bond cleavage and subsequent ring closure of the resulting aryl allyl carbonium ion. This process is favored by electron-donating groups X(OCH₃, CH₃) which stabilize the carbonium ion and catalysts of low α-hydrogen abstraction strength (i.e., low Bi). Bismuth has been shown to enhance the rate of α-hydrogen abstraction in σ-O



SCHEME 1. Mechanism of Allylbenzene Oxidation.

allyl molybdates (*8*). Cinnamaldehydes are formed via a second allylic H abstraction, a process favored by catalysts of high H-abstracting strength (i.e., high Bi) and electron-withdrawing groups. This is consistent with the experimental results, for MoO_3, $Bi_2Mo_3O_{12}$, and Bi_2MoO_6 in which *p*-methoxyallylbenzene over MoO_3 gives the highest indene selectivity (71.5%), while *p*-chloroallylbenzene over Bi_2MoO_6 gives the highest selectivity to cinnamaldehyde (86.8%). Thus, the overall rate of the catalytic oxidation of $pXC_6H_4CH_2CH{=}CH_2$ is controlled by radical substituent effects ($X = OCH_3 > Cl > CH_3 > H$), while the selectivity to indene is controlled by cationic substituent effects ($X = OCH_3 > CH_3 > H > Cl$).

In terms of the selective oxidation of propylene over bismuth molybdate catalysts, these results are consistent with the formation of a radical-like π-allyl complex in the initial rate-determining H abstraction, and reconfirm the mechanism formulated on the basis of previous studies (*8*, *9*).

REFERENCES

1. Kraus, M., *in* "Advances in Catalysis and Related Subjects" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 17, p. 75. Academic Press, New York, Academic Press, New York, 1967; Kraus, M., and Kochloefl, K., *Collect. Czech. Chem. Commun.* **32,** 2320 (1967); Kraus, M., *Collect. Czech. Chem. Commun.* **34,** 699 (1969).
2. Adams, C. R., and Jennings, T. J., *J. Catal.* **3,** 549 (1964); **2,** 63 (1963).
3. Adams, C. L., *in* "Proceedings, 3rd International Congress on Catalysis (Amsterdam 1964)," p. 240. North-Holland, Amsterdam, 1965.
4. Bandlish, R. K., Garner, A. W., Hodges, M. L., and Timberlake, J. W., *J. Amer. Chem. Soc.* **97,** 5856 (1975).
5. Greene, F. D., Burrington, J. D., and Karkowski, A. M., *in* "Organic Free Radicals" (W. A. Pryor, Ed.), ACS Symposium Series 69; p. 122. Amer. Chem. Soc., Washington, D.C., 1978.
6. Shelton, J. R., and Liang, C. K., *J. Org. Chem.* **38,** 2301 (1973).
7. Sosin, S. L., Korshak, V. V., and Val'kovskii, D. G., *Dokl. Acad. Nauk. SSSR* **155,** 376 (1964).
8. Burrington, J. D., Kartisek, C. T., and Grasselli, R. K., *J. Catal.* **63,** 235 (1980).
9. Burrington, J. D., and Grasselli, R. K., *J. Catal.* **59,** 79 (1979).

J. D. BURRINGTON
C. T. KARTISEK
R. K. GRASSELLI

Research Department
The Standard Oil Company (Ohio)
4440 Warrensville Center Road
Warrensville Heights, Ohio 44128

Received January 4, 1980; revised January 21, 1981