BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2502—2505 (1969)

Catalytic Vapor-Phase Ammoxidation of Substituted Toluenes over Chromium Oxide[1]

Katsumasa SAKANISHI and Yoshiro OGATA

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya

(Received March 1, 1969)

Ammoxidation of substituted toluenes over a chromium oxide catalyst has been studied in a flow system at atmospheric pressure. The reactions give satisfactory yields (*ca.* 70%) of corresponding nitriles at high conversion of toluenes. The rate constant for the reaction of substrate adsorbed on the catalyst surface, k_T^0, is independent of the substituent of substrate, while the adsorption equilibrium constant of gaseous substrate, K_T, depends on the substituent, affording Hammett's ρ of -0.9 for σ^+. These results support our mechanism reported previously for the analogous oxidation of toluene and ethylbenzene over Cr_2O_3, which involves an electron transfer from adsorbed hydrocarbons to dissociated oxygen.

In previous papers, we have reported the kinetic study on the ammoxidation of toluene[2] and ethylbenzene[3] over chromium oxide and interpreted the results in terms of the Langmuir-Hinshelwood mechanism.[2,3] The rate constant for the reaction of substrate on the catalyst surface, $k°$, and the adsorption equilibrium constants, K, were estimated and it is proposed that the rate-determining step is the reaction between adsorbed hydrocarbon and adsorbed oxygen in a dissociated form.[3] The present paper is an extention of the study to the ammoxidation of substituted toluenes over chromium oxide; the reaction gave satisfactory yields of substituted benzonitriles, the data being interpreted in terms of $k°_T$ and K_T.

Experimental

Materials. Toluene (bp 110.6°C), ethylbenzene (bp 135.8—136.0°C), *o*-xylene (bp 144.0—144.5°C), *m*-xylene (bp 137.2—137.5°C) and *p*-xylene (bp 136.5—137.0°C) were purified as previously described.[2,3] *p*-*t*-Butyltoluene (bp 108.5°C/60 mmHg) was purified by rectification. Commericial *o*-chlorotoluene was employed. *m*-Chlorotoluene (bp 59.5—61.0°C/23 mmHg),[4] *p*-chlorotoluene (bp 160.8—161.1°C),[5] *o*-bromotoluene (bp 76.5—77.7°C/23 mmHg),[6] *m*-bromotoluene (bp 104°C/65 mmHg),[7] *p*-bromotoluene (bp 79.5—79.9°C/24 mmHg),[8] *o*-tolunitrile (bp 93—94°C/20.5 mmHg),[9] *m*-tolunitrile (bp 104—104.5°C/24 mmHg),[9] and *p*-tolunitrile (bp 105.5°C/23 mmHg)[9] were synthesized by well-known methods. Commercial ammonia, N_2 and O_2 were employed. The same catalyst as that in the previous papers[2,3] was used for kinetic studies. The catalyst of 5 wt% Cr_2O_3 on Al_2O_3, used for synthetic studies, was prepared by a method similar to that in the previous paper[2] and was allowed to age under reaction conditions for 35 hr in order to stabilize its activity.

Apparatus and Procedures. The apparatus and procedure for kinetic studies were similar to those employed before,[2] but a column of 30 wt% Silicone D.C. 550 on Chamelite CK 40 cm was used for gas chromatographic analysis of the substituted toluenes.

For synthetic purposes, a reactor of stainless steel, 19 mm inner diameter, with a concentric thermowell

---

[1] Contribution No. 134.

[2] Y. Ogata and K. Sakanishi, *Tetrahedron*, **24**, 4881 (1968).

[3] K. Sakanishi and Y. Ogata, *ibid.*, 6277.

[4] F. Reverdin and P. Crepieux, *Chem. Ber.*, **33**, 2505 (1900).

[5] C. S. Marvel and S. M. McElavain, "Organic Syntheses," Coll. Vol. I (1956), p. 170.

[6] L. A. Bigelow, *ibid.*, p. 135.

[7] L.A. Bigelow, J. R. Johnson and L. T. Sandborn, *ibid.*, p. 133.

[8] L. A. Bigelow, *ibid.*, p. 136.

[9] H. T. Clark and R. R. Read, *ibid.*, p. 514.

(4 mm outer diameter), was immersed in a thermostated alkali nitrates bath. The substrates of *ca.* 2 m*l* were charged by a microfeeder, and introduced with the mixed reaction gas into the reactor for about 2 hr. When the reaction was over, N_2 gas was fed into the ractor for 30 min. The products were collected by a trap cooled by air and traps cooled by a freezing mixture. Recrystallized products were identified by means of their melting points as well as GLC analysis.

Results

Preparative Ammoxidation of Substituted Toluenes. Ammoxidation of substituted toluenes[10] to prepare benzonitriles were carried out over the stabilized catalyst of 40 m*l* at the standard composition of reaction gas, *i. e.*, partial pressure of substrate (p_T) was 1.3×10^{-2} atm, that of oxygen (p_O) 13.3×10^{-2} atm, and that of ammonia (p_A) 6.7×10^{-2} atm. Nitrogen gas was used as a diluent.

TABLE 1. AMMOXIDATION OF SUBSTITUTED TOLUENES AT BATH TEMPERATURE OF 370°C WITH GAS SPACE VELOCITY OF 450 hr^{-1}

Substrate	Product	Yield (mol %)[a]
p-Chlorotoluene	*p*-Chlorobenzonitrile	68
m-Chlorotoluene	*m*-Chlorobenzonitrile	69
o-Chlorotoluene	*o*-Chlorobenzonitrile	72
p-Bromotoluene	*p*-Bromobenzonitrile	75
m-Bromotoluene	*m*-Bromobenzonitrile	69
o-Bromotoluene	*o*-Bromobenzonitrile	74
p-Tolunitrile	Terephthalonitrile	66
m-Tolunitrile	Isophthalonitrile	63
o-Tolunitrile	Phthalonitrile +Phthalimide	36 15
p-Xylene	Terephthalonitrile	45
m-Xylene	Isophthalonitrile +*m*-Tolunitrile	29 5.6
o-Xylene	Phthalonitrile +Phthalimide	26 10
Toluene	Benzonitrile	45
Toluene[b]	Benzonitrile	72
Ethylbenzene	Benzonitrile +Styrene	36 8.2
Ethylbenzene[c]	Benzonitrile +Styrene	50 20

a) Based on the fed substrate. The conversions of all substrates were 100%, except for footnote b and c.

b) The conversion of toluene was 86% at bath temperature of 356°C, with gas space velocity of 930 hr^{-1} and catalyst volume of 19.3 m*l*.

c) The conversion of ethylbenzene was 77% at bath temperature of 360°C with gas space velocity of 930 hr^{-1} and catalyst volume of 19.3 m*l*.

As shown in Table 1, *o*-, *m*- and *p*-chlorotoluenes, bromotoluenes, and *m*- and *p*-tolunitriles gave fairly high yields of corresponding nitriles (*ca.* 70%). Relatively low yields of nitriles were obtained in ammoxidation of xylenes and unsubstituted toluene at 370°C under these conditions. However, at moderate reaction conditions (footnotes b and c in Table 1), toluene gave higher yield of benzonitrile (72%), its selectivity being 84%, while ethylbenzene gave 50% benzonitrile and 20% styrene, their selectivities being 65% and 26%, respectively.

Kinetics of Ammoxidation of Substituted Toluenes. The reaction conditions for kinetics were as follows: p_T, $0.67-2.67\times10^{-2}$ atm; p_A, 6.7×10^{-2} atm; p_O, 13.3×10^{-2} atm; reaction temperature, 400°C; catalyst volume, 2.5 m*l*; and gas space velocity, 7200 hr^{-1}.

Treatment of experimental data was similar to that of our previous reports,[2,3] *i. e.*, the rate of consumption of substrate, v_T, is expressed as:

$$v_T = -\frac{d[\text{substrate}]}{dt} = -\frac{d\left(\dfrac{p_{T_0}(1-x_T)}{RT_0}\right)}{d\left(\dfrac{V}{F}\right)}$$

$$= k_T p_T{}^t \cdot p_O{}^n \cdot p_A{}^a \tag{1}$$

$p_O > p_T$ and $p_A > p_T$, and hence p_O and p_A are virtually constant under experimental conditions. Therefore, integration of Eq. (1) leads to

$$p_{T_0}\cdot x_T \simeq k_T RT_0 p_{T_0}{}^t \cdot p_0{}^n \cdot p_A{}^a (V/F) \tag{2}$$

or

$$v_T \simeq \frac{p_{T_0}\cdot x_T}{RT_0\left(\dfrac{V}{F}\right)} \tag{3}$$

Hence, the t value (kinetic order in substrate) can be estimated from the slope of line in the plot of log ($p_{T_0}x_T$) *vs.* log (p_{T_0}). Also, applying Langmuir-Hinshelwood mechanism, v_T is expressed as follows.[2,3]

$$v_T = k_T{}^\circ \frac{K_T p_0 \sqrt{K_O p_O}}{(1 + K_T p_{T_0} + \sqrt{K_O p_O})^2} \tag{4}$$

Introduction of Eq. (3) into Eq. (4) gives

$$x_T{}^{-1/2} = \{1 + \sqrt{(K_O p_O)} + K_T p_{T_0}\} \times \{k^\circ{}_T RT_0 K_T \sqrt{(K_O p_O)}V/F\}^{-1/2} \tag{5}$$

Relative values of K_T and $k^\circ{}_T$ can be obtained by means of the plot of $x_T{}^{-1/2}$ *vs.* p_{T_0} at various p_{T_0} with constant and known p_O, p_A and V/F as shown in Fig. 1. Values of K_O and $k^\circ{}_T RT_0$ were estimated by using the value of 0.15 atm^{-1} for K_O, as obtained previously.[2]

These values are shown in Table 2. The values of K_T, $k^\circ{}_T RT_0$ and t were comparable with those obtained previously.[2] The values of $k^\circ{}_T RT_0$ are

---

[10] For literature on ammoxidation of halotoluenes, see U. S. Pat. 2499055 (1950); German Pat. 1189976 (1965); and for *p*-*t*-butyltoluene, see S. D. Mekhtiev, R. G. Rizaev and A. S. Movruzova, *Dokl. Akad. Nauk Azerb. SSR*, **21**, (5), 17 (1965); E. Fischer, *Chem. Ingr.-Tech.*, **38**, 1203 (1966); and for a mixture of *m*-tolunitrile and *m*-xylene, see S. D. Mekhtiev, G. N. Suleimanov, Sh. F. Sharifova and Kh. S. Samedov, *Azerb. Khim. Zh.* (5), 73 (1966).

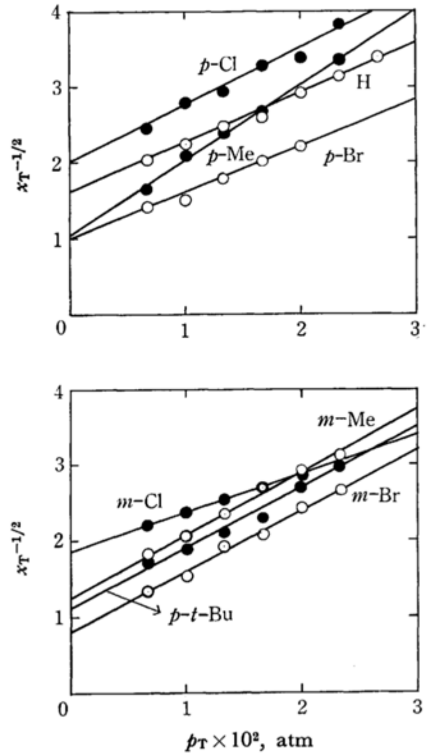

Fig. 1. Calculations of K_T and k°_T at 400°C by means of Eq. (5).

TABLE 2. KINETIC PARAMETERS IN AMMOXIDATION OF SUBSTITUTED TOLUENES AT 400°C

Substituent	Conversion[a] (mol %)	K_T[b] (atm^{-1})	$k^\circ RT_0$[b] (10^2 atm hr^{-1})	t[c]
p-CH$_3$	14.5	107	5.6	−0.1
p-t-Bu	16.7	72	6.2	∼0
m-CH$_3$	13.9	77	5.4	0
H	14.8	48	5.6	+0.42
p-Cl	9.2	43	4.0	$+0.4_0$
m-Cl	13.9	31	6.3	$+0.5_2$
p-Br	24.3	63	11.0	-0.1_5
m-Br	22.8	114	9.3	−0.3

a) At p_{T_0} of 16.7×10^{-2} atm
b) Calculated by using $K_O=0.15$ atm^{-1}, see Ref. 2
c) Kinetic order in substrate

nearly constant except bromotoluenes. Values of K_T depend on the substituent of toluene. Hammett's plot of log K_T *vs.* Brown's σ^+ gave a straight line, from which the ρ value was estimated to be −0.9, except for bromotoluenes.

Discussion

Since the selectivities to nitriles are high at moderate reaction conditions (Table 1), kinetic data can clarify the mechanistic feature of the ammoxidation of substituted toluenes to the corresponding nitriles. As suggested previously,[3] the mechanism for the oxidation would be expressed as follows, where the rate is determined by step 8 or 9:

$$\text{Hc (gas)} + \text{Catalyst}^+ \overset{K_{Hc}}{\rightleftarrows} \text{Hc}^+\text{(ads)} + \text{Catslyst} \tag{6}$$

$$\text{O}_2\text{ (gas)} + 2\text{ Catalyst} \overset{K_O}{\rightleftarrows} 2\text{O}^-\text{(ads)} + 2\text{Catalyst}^+ \tag{7}$$

$$\text{Hc}^+\text{(ads)} + \text{O}^-\text{(ads)} \underset{k_{-8}}{\overset{k_8}{\rightleftarrows}} [\text{Hc}^+\text{(ads)O}^-\text{(ads)}] \quad \text{I (transition state)} \tag{8}$$

$$[\text{Hc}^+\text{(ads)O}^-\text{(ads)}] \xrightarrow{k_9} \text{Intermediates or Products} \tag{9}$$

Here Hc means hydrocarbon and (ads) means adsorbed gas on the catalyst. Hence, $K_{Hc}\equiv K_T$ and $k^\circ_T\equiv k_8\cdot k_9/k_{-8}+k_9$.

The effect of substituent of toluenes on K_T gives ρ of −0.9 and the effect is expected from Eq. (6), where adsorbed hydrocarbons act as electron-donors to the catalyst. The relation between t and K_T in Table 2 implies that the stronger adsorption of substrate corresponds to the lower reaction order substrate.[3]

Equation (9) may be a hydrogen abstraction reaction. Factors influencing the selectivity in the hydrogen abstraction reaction are (i) the bond dissociation energy of the breaking C–H bond, (ii) the ionization potential of the formed radical, and (iii) the factor of entropy.[11] The transition state, I, seems to be resonating as follows.

$$\underset{\text{II}}{[\text{(ads)}^+\text{ArCH}_2\text{:H}\cdot\text{O}^-\text{(ads)}]} \leftrightarrow \underset{\text{III}}{[\text{(ads)}^+\text{ArCH}_2\cdot\dot{\text{H}}\cdot\text{O}^-\text{(ads)}]} \leftrightarrow \underset{\text{IV}}{[\text{(ads)}^+\text{ArCH}_2{}^+\dot{\text{H}}\text{:}^-\text{O}^-\text{(ads)}]} \tag{10}$$

However, the contribution of the carbonium ion-type structure, IV, to stabilize the transition state may be negligible. Hence, the ionization potential of the substituted benzyl radical is not important for the reactivity of substrate. The bond dissociation energies of the substituted benzylic C–H bonds are almost constant.[12,13] Therefore, if the factor of entropy and others are nearly constant, $k^\circ_T\boldsymbol{R}T_0$ would not be affected by substituents. As shown in Table 2, the observed values of $k^\circ_T\boldsymbol{R}T_0$ are almost independent of substituent, except bromotoluene. This substituent effect on $k^\circ_T\boldsymbol{R}T_0$ and K_T supports the mechanism shown in Eqs. (6)—(9).

---

[11] H. Sakurai and K. Tokumaru, "Chemistry of Free Radicals," Nankodo Ltd., Tokyo (1967), Chap. 17

[12] M. Szwarc, *Chem. Rev.*, **47**, 75 (1950).

[13] T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd. Ed., Butterworths Scientific Publ., London (1958).

The unusual behavior of bromotoluenes may be explained as follows: The adsorption of substrates seems to need the charge transfer of π-donor type involving π- or pseudo π-electron and/or the charge transfer of n-donor type involving lone pair electron; in bromotoluenes, the latter may be more important and change the factor of entropy. Further, the decomposition of bromotoluenes may cause the intervention of Br$\cdot$ in the reaction system.[14]

Nomenclature

A	Ammonia
O	Oxygen
T	Substrate, *i. e.*, substituted toluenes
a, n, and t	Kinetic orders in A, O and T, respectively
p_T, p_O and p_A	Partial pressures of subscripted substance
0	Subscript 0 means initial stage of reaction
v_T	Rate of consumption of substate, mol $\mathrm{m}l^{-1}$ hr^{-1}
k°_T	Rate constant for the reaction of substrate on catalyst surface
x_T	Conversion of substrate, mol mol^{-1}
K_i	Adsorption equilibrium constant of i gas, atm^{-1}
V	Volume of catalyst, ml
F	Flow rate of gas (STP), ml hr^{-1}

The authors are indebted to Dr. T. Morimoto for the materials, and to Nissan Chem. Ind. Co. and Seitetsu Chem. Ind. Co. for their aid in the experiments.

---

[14] K. Tarama, K. Hattori and Y. Kobayashi, Preprints for the 17th Annual Meeting of the Chemical Society of Japan (Tokyo, April 1964), p. 336.