3442 © 1991 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, ***64***, *3442—3444 (1991)* [Vol. 64, No. 11

Effect of Anions on the Epoxidation of Styrenes with H_2O_2 in the Presence of Ammonium Heptamolybdate(VI)-Dioctyltin Oxide Catalysts

Masami Inoue,* Eiichi Nakayama, Yuuko Nakamura,
Seichi Rengakuji, and Keiichi Nishibe
Faculty of Engineering, University of Toyama,
Gofuku, Toyama 930

(Received May 18, 1991)

The epoxidation of styrene, α-methylstyrene, β-methylstyrene, *p*-chlorostyrene, and *m*-divinylbenzene with H_2O_2 in the presence of ammonium heptamolybdate(VI)–dioctyltin oxide catalysts in $CHCl_3$–H_2O was studied. The addition of neutral salts, such as $NaNO_3$ or Na_2SO_4, to the catalyst system prevented the successive hydration of styrene oxide once formed. The presence of KCl or NaCl almost suppressed the oxidation, while no substantial effect was observed in $NaClO_4$. The various effects of these anions were related to the results concerning the coordination of anions to Mo(VI)-ions.

The epoxidation catalysts and agents for alkenes provided various kinds of epoxides.[1] Among those, styrene oxide and its derivatives are useful materials for polymer chemistry and organic synthesis. The use of aqueous H_2O_2 as an oxidation agent is easy to handle and clean since H_2O_2 is reduced to give water. In our present reaction conditions, the hydration of styrene oxide to 1-phenyl-1,2-ethanediol was a chief side reaction.

Previously, we proposed ammonium heptamolybdate(VI)–dioctyltin oxide catalysts for the selective epoxidation of styrene as well as aliphatic alkenes with H_2O_2 in $CHCl_3$–H_2O.[2] In this two-layer solvent system, a longer reaction time (24 h) decreased the yield of styrene oxide after reaching a maximal yield. During the investigation of the effect of anions on the catalytic activity, we found that the addition of a small amount of neutral salts, such as $NaNO_3$ or Na_2SO_4, prevented the hydration of styrene oxide. On the other hand, in the case of KCl and NaCl, the rate of oxidation was decreased remarkably.

In this report, the epoxidation of styrene, α-methylstyrene, β-methylstyrene, *p*-chlorostyrene, and *m*-divinylbenzene was carried out and the effect of anions was studied from the standpoint of the activity of catalysts and the selectivity in epoxide formation.

Experimental

Materials. Styrene (Wako Pure Chemicals Co.), α-methylstyrene, β-methylstyrene, *p*-chlorostyrene, *m*-divinylbenzene (Tokyo Kasei Co.), and dioctyltin oxide (Kyodo Yakuhin Co., Tokyo) were used as received. Aqueous 60% H_2O_2 was kindly supplied from Tokai Denka Kogyo Co., Tokyo. KCl was used after twice recrystallizations. Neutral salts and other materials of GR grade were used for this experiment.

General Procedures. In a 300 ml round-bottom flask equipped with a condenser, the catalyst was prepared in situ by mixing ammonium heptamolybdate(VI) (0.57 mmol), neutral salts (4.8 mmol in H_2O 8.0 ml), and dioctyltin oxide (8.0 mmol). The reaction was carried out by the addition of $CHCl_3$ (8 ml), styrenes (350 mmol), and H_2O_2 (318 mmol) under stirring with TEFLON (poly(tetrafluoroethylene))-covered magnetic stirring bar at 30 °C in a thermostatted water bath. Dioctyltin oxide, dispersed in $CHCl_3$, gradually dissolved and the reaction was started. At intervals, a small portion (0.5 ml) was pipetted out of the $CHCl_3$-layer and diluted with $CHCl_3$ (5 ml). To the solution was added *m*-xylene in acetonitrile solution (0.5 ml) as an internal standard.

Gas-liquid chromatography (GLC) was carried out on a Shimadzu GC-8A instrument using a glass column (2 m) packed with a 2%-Silicone OV-17 (2 m) under programmed oven temperature from 50 to 150 °C (3 °C min^{-1}). In the case of divinylbenzene, the temperature range from 50 to 230 °C (4 °C min^{-1}) was used. In the preparation of authentic epoxides, styrene, α-methylstyrene, β-methystyrene, *p*-chlorostyrene, and *m*-divinylbenzene were oxidized with *m*-chloroperbenzoic acid (mcpba) according to a method described in the literature,[3] and the corresponding epoxides were obtained by column chromatography (Kieselgel 60, Merck Co.) with pentane followed by pentane–diethyl ether (2:1) as eluents. The purities of these epoxides were 85 to 95% according to GLC analysis. The *m*-divinylbenzene monoepoxide separated from the solution was unstable and polymerized upon standing at room temperature for a few days.

Results and Discussion

Effect of Salts in the Epoxidation of Styrene. The oxidation of styrene with H_2O_2 was carried out in a two-phase solvent of $CHCl_3$–H_2O in the presence of ammonium heptamolybdate(VI)–dioctyltin oxide and an equivalent amount of such neutral salts as $NaNO_3$, Na_2SO_4, $NaClO_4$, KCl, or NaCl to Mo(VI) ions. In the absence of salts, the yield of styrene oxide reached a maximum of 60% after 8 h; further reaction (24 h) gradually decreased the yield to as low as a 34%.

Figure 1 shows the time course of the epoxidation of styrene with H_2O_2 in the presence of various salts. The addition of these salts changed the color of the aqueous layer from yellow to orange. When such salts as Na_2SO_4 or $NaNO_3$ were added, the hydration of styrene oxide, once formed, was delayed.

Unexpectedly, although the addition of NaCl and KCl

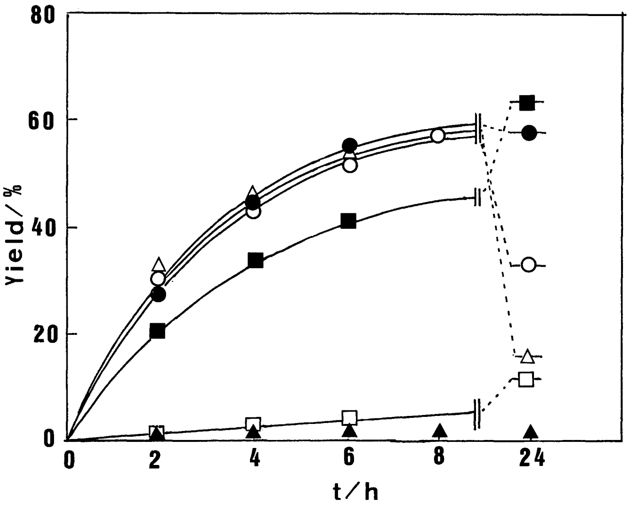

Fig. 1. Effect of salts in the epoxidation of styrene (**1**) at 30 °C. ○; none ●; Na_2SO_4, ■; $NaNO_3$, △; $NaClO_4$, □; KCl, ▲; NaCl. **1** (43.7 mmol), 60% H_2O_2 (39.7 mmol), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.07 mmol), dioctyltin oxide (1.0 mmol), salts (0.6 mmol in H_2O 1 ml), and $CHCl_3$ (5 ml) were used. Yield were based on H_2O_2.

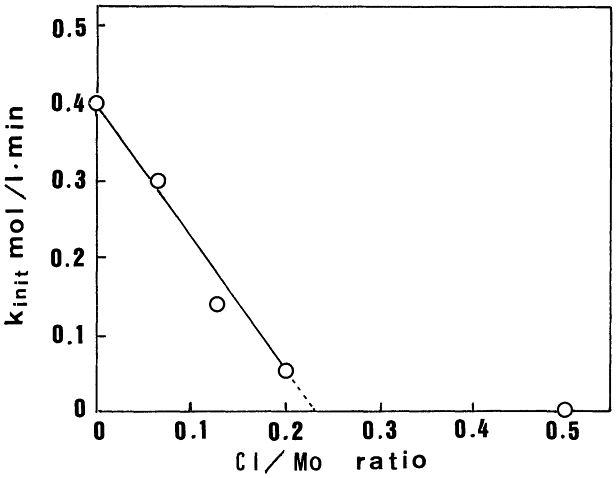

Fig. 2. Relation between the initial rate of the epoxidation of styrene (**1**) and the ratio of Cl^- to Mo(VI) ion.[a)]
a) **1** (350 mmol), 60% H_2O_2 (318 mmol), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.57 mmol), dioctyltin oxide (8 mmol), KCl (8 mmol in H_2O 8 ml), and $CHCl_3$ (40 ml) were used. Reactions were carried out at 30 °C.

Table 1. Initial Rate of the Epoxidation of Styrene (**1**) in the Presence of Various Salts[a)] at 30 °C

Salts	Initial rate $mol\ l^{-1}\ s^{-1}$
None	2.9×10^{-2}
ClO_4^-	2.8×10^{-2}
SO_4^{2-}	1.6×10^{-2}
NO_3^-	1.3×10^{-2}
Cl^-	ca. 0

a) **1** (350 mmol), 60% H_2O_2 (318 mmol), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.57 mmol), dioctyltin oxide (8 mmol), salts (4.8 mmol in H_2O 8 ml), and $CHCl_3$ (40 ml) were used.

strongly suppressed the oxidation, the presence of NaBr and NaI decomposed H_2O_2 vigorously. In the case of $NaClO_4$, no substantial effect upon the yield of epoxide was observed.

Phenylacetaldehyde as a by-product was not found in our reaction products when GLC was carried out on a glass column packed with PEG (2m) with the programmed oven temperature from 50 to 150 °C (3 °C min^{-1}).

The effect of salts was confirmed quantitatively by taking the initial rates for the oxidation to styrene oxide (Table 1). In all experiments, the selectivities to styrene oxide were >90%, except during the initial stage of a reaction lower than 10% conversion. The rates of epoxidation considerably differed depending on the kinds of anions, as shown by the following order:

$$H_2O,\ ClO_4^- > SO_4^{2-} > NO_3^- > Cl^-.$$

This tendency, except for ClO_4^-, was in accord with that of well-known spectrochemical series observed in the spectral shifts of metal complexes in the presence of various anions.[4)] Although the precise structure of Mo(VI) complexes in solution is still unknown, it was supposed that anions such as SO_4^{2-}, NO_3^-, or Cl^- are tightly coordinated on Mo(VI) ions and affected both the oxidation of styrene and the hydration of styrene oxide by decreasing the Lewis acidity of the catalyst. From a practical standpoint, the addition of Na_2SO_4 or $NaNO_3$ is usable as a kind of stabilizer of styrene oxide.

It was interesting that the addition of KCl to Mo(VI) ions in a 1:1 ratio almost suppressed the oxidation. The oxidation rate was decreased in proportion to the amount of KCl to Mo(VI) ions. Figure 2 shows a linear relationship between the initial rate of the oxidation and the amount of KCl to Mo(VI) ions. The extrapolation of the rate of oxidation to zero velocity gave the ratio of KCl:Mo(VI) ion =1:4.

Therefore, from the obtained results, two possible cases were considered. In the first, the amount of active species was only 1/4 of ammonium heptamolybdate(VI) used. The other case was that one active complex molecule was formed from four Mo(VI) ions. In any case, tightly coordinated Cl^- on Mo(VI) ions decreased the activity for the oxidation of styrene. From the obtained results, we supposed that these anions, except ClO_4^-, are also coordinated on Mo(VI) ions as a ligand.

Effect of Salts in the Epoxidation of Styrene Derivatives. The effect of salts on the stabilization of epoxide was also examined for several styrene derivatives. As shown in Table 2, the addition of $NaNO_3$ also stabilized *β*-methylstyrene oxide and *m*-divinylbenzene monoepoxide. On the other hand, under our reaction conditions,

Table 2. Effect of $NaNO_3$ on the Epoxidation of Styrene Derivatives with H_2O_2[a)]

Styrenes	Temp.	Salts	Time	Yield	Time	Yield
	°C		h	%	h	%
Styrene	30	$NaNO_3$	12	60.4	24	52.0
		None		61.7		25.8
p-Chlorostyrene	30	$NaNO_3$	10	42.5	24	57.1
		None		58.1		71.4
α-Methylstyrene	35	$NaNO_3$	10	46.3	24	54.3
		None		52.1		58.6
β-Methylstyrene	30	$NaNO_3$	10	52.8	24	76.5
		None		67.1		47.9
m-Divinylbenzene	40	$NaNO_3$	6	57.5[b,c)]	8	56.2[b,e)]
		None		40.3[b,d)]		10.5[b,f)]

a) Styrenes (4.3 mol l^{-1} $CHCl_3$), styrenes : 60% H_2O_2 : $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$: Oct_2SnO : $NaNO_3$=100 : 100 :1 : 2 : 1. b) Yield of monoepoxide. c) Diepoxide 9.9%. d) Diepoxide 1.8%. e) Diepoxide 5.4%. f)No diepoxide was detected.

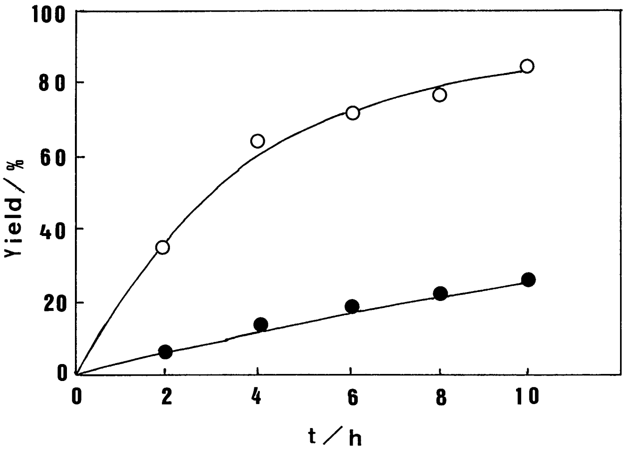

Fig. 3. Effect of stirring on the epoxidation of styrene (**1**) at 30 °C,[a)] ○; under stirring, ●; without stirring, a) **1** (394 mmol), 60% H_2O_2 (187 mmol), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.57 mmol), dioctyltin oxide (8 mmol), $NaNO_3$ (4.8 mmol in H_2O 5 ml), and $CHCl_3$ (45 ml) were used. Yields were based on H_2O_2.

α-methylstyrene oxide and *p*-chlorostyrene oxide, once formed, were sufficiently stable, even under a lack of such salts as $NaNO_3$ or Na_2SO_4. In the case of *m*-divinylbenzene, the oxidation was almost stopped when one of two vinyl groups was oxidized.

The effect of the concentration of styrene or H_2O_2 upon the epoxidation rate also gave information concerning the Mo(VI) complexes under oxidation: The rates were approximately first-order with respect to both the styrene and H_2O_2 concentrations. Therefore, the coordination of these substrates to Mo(VI) ions might be very weak. The stirring procedure (150 rpm) increased the oxidation rate by as large as 6 times (Fig. 3). The evaporation of water from the aqueous layer of the reaction solution gave ammonium heptamolybdate(VI) as yellow crystals, while a pale-yellow syrup of organotin compounds was obtained from the $CHCl_3$ layer. However, both of the separated compounds were inactive for epoxidation.

In our catalyst system, the instability of styrene oxide and the denaturalization of Mo(VI) complexes were serious drawbacks. The former could be improved with a slight sacrifice of the catalyst activity by the addition of salts, such as $NaNO_3$ or Na_2SO_4.

The present work was supported in part by The Tamura Foundation for Encouragement of Science and Technology.

References

1) K. A. Joergensen, *Chem. Rev.*, **89**, 431 (1991).

2) T. Kamiyama, M. Inoue, H. Kashiwagi, and S. Enomoto, *Bull. Chem. Soc. Jpn.*, **63**, 1559 (1990).

3) M. Imuta and H. Ziffer, *J. Org. Chem.*, **44**, 1351 (1979).

4) R. Tsuchida, M. Kobayashi, and S. Yamada, *Bull. Chem. Soc. Jpn.*, **13**, 388 (1938).