Amine acceleration of oxidation of styrene epoxide with oxygen in acidic media

L. V. Petrov^{*} and V. M. Solyanikov

Institute of Problems of Chemical Physics, Russian Academy of Sciences, 1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 (496) 522 3507. E-mail: plv@icp.ac.ru

Additives of aromatic amines (aniline, α -naphtylamine, *o*-, *p*-, and *m*-aminophenols) accelerate the low-temperature (343 K) molecular oxygen uptake by styrene epoxides in acetonitrile solution of toluenesulfonic acid. Amines decrease the output of benzaldehyde (oxidation product) and nearly suppress the formation of phenylacetaldehyde, the product of acid-catalyzed conversion of styrene epoxide.

Key words: styrene epoxide, *p*-toluenesulfonic acid, aromatic amines, oxidation, molecular oxygen, aromatic aldehydes.

Aromatic amines are widely used as clock antioxidative stabilizers of petroleum products. In scientific practice amine inhibitors were applied, in particular, for measuring formation (initiation) rates of free radicals when inhibitor traps, in particular, free peroxide radicals, suppress oxidation, and are thus consumed. The initiation rate was calculated from the consumption rate. In the course of experimental search for an inhibitor, trap for a radical particles involved in the oxidation with oxygen of a binary system (BS), styrene epoxide (1)—*p*-toluenesulfonic acid (2),¹ we found that the addition of the strong inhibitor α -naphthylamine (3) to the oxidized BS 1—2 in MeCN solution accelerates the O₂ uptake rather than sup-



presses it. The enlargement of the range of objects of the search showed that all tested aromatic amines, viz., p- (4), o- (5), and *m*-aminophenols (6), accelerate oxidation by their addition to BS 1–2. The simplest aromatic amine, aniline (7), when introduced into the system, also enhances the oxidation rate of BS 1–2. The oxidation of *para*-halogen-substituted *p*-chloro- (8) and *p*-fluoro-styrene (9) epoxides was also accelerated in the presence of compound 7. In a mixture of Bu^tOH (90%) and chlorobenzene (10%) (vol/vol) often used by us, 1-4 the introduction of amine 3 accelerates the oxidation of compound 1 in the presence of 2. Finally, the acceleration effect is pronounced in the absence of acid 2 in a combined solution of amines, epoxides, and glacial AcOH.

Experimental

Experiments were carried out with thoroughly purified nitrogen bases. Aniline (7) and pyridine (10) were purified by rectification, and after rectification they were colorless transparent liquids. Amine 3 was purified by recrystallization from *n*-decane to obtain needle-like weakly lilac crystals. Compounds 1, 2,² AcOH, Bu^tOH, and PhCl were purified using standard approved procedures.

Acetonitrile (Acros Organics, for HPLC UV) with a passport water content of $2.5 \cdot 10^{-3}$ mol L⁻¹ was used without additional purification, as well as compounds **8** and **9** (Aldrich, with a purity of 96 and 95%, respectively). The O₂ uptake rates (oxidation rates) *V* in quartz one-compartment reactors of the manometric system were measured changing the earlier¹ described procedure of filling with O₂ with preliminary evacuation of the frozen solution. The working solution in the reactor was thoroughly purged with oxygen at ~20 °C, the reactor was mounted into the system already filled with O₂, and heating and shaking of the reactor and stop-watch were switched on. The heating duration of the solution was 120–180 s and, therefore, the ex-

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Fig. 1. Kinetic curves of the oxygen uptake by binary system 1-2(I), ternary system 7-1-2(2), pair 7-1(3), pair 7-2(4), and oxidate of the experiment (curve 4) after introduction of compound 1 (5); MeCN, 343 K, $[1]_0 = 0.52$ mol L⁻¹, [2] = 0.034 mol L⁻¹, and [7] = 0.44 mol L⁻¹.

perimental uptake curves (Fig. 1, curves I-5) did not start from zero.

The quantitative analysis of styrene epoxide, benzaldehyde, and phenylacetaldehyde was performed by HPLC using a GPTs liquid chromatograph (Czechia). Standard glass columns were Separon SGX CN (150×3 mm), standard eluent was *n*-heptane—2-propanol (0.1 vol.%), an LCD 2563 was a detector (UV-254), flow rates were 0.3-0.8 mL min⁻¹, volumes of introduced samples were 0.25-0.5 µL, and chlorobenzene was an internal standard.

Results and Discussion

The data presented in Table 1 indicate the abundance of the phenomenon of acceleration by amines of the oxygen uptake by the epoxide—acid BS. Therefore, in terms of the earlier formed concepts, one can speak about a new ternary system (TS) amine-epoxide-acid; we have previously¹⁻⁴ studied TS RH-1-2, ROOH-1-2, and Bu^tOCl-1-2. The "doubled" experiments (see Table 1, entries 3, 3', 4, 4', etc.), i.e., experiments with the introduction of a lacking component of the TS into the oxidate of the previous two-component solution, were carried out to reveal the possible participation in the acceleration of oxidation or reactions of pairs of components or pairs of reaction products. For instance, the possibility of oxidation of individual amine in an acidic medium or the easy oxidizability of the reaction products of amines with accumulated benzaldehyde (11) and phenylacetaldehyde (12) can be assumed.⁵



The procedure of our search for objects of studying the mentioned above phenomenon is illustrated by the data in Fig. 1. The slope angle of curve 1 characterizes the oxidation rate $(\tan_I = V_I = V_{BS} = 14 \cdot 10^{-6} \text{ mol } \text{L}^{-1} \text{ s}^{-1})$ of the well studied earlier BS 1-2. The introduction of third component 7 into the initial solution doubles the oxidation rate, $V_{\text{TS}} = V_2 = 28 \cdot 10^{-6} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$ (see Fig. 1, curve 2). An assumption that an increase in the rate, being a consequence of the fast oxidation of combined solution 1+7 (see Fig. 1, curve 3) or compound 7 in an acidic medium (see Fig. 1, curve 4), is poorly probable: the sum of oxidation rate of pairs of components of TS in entries 3 and 4 (see Fig. 1) is only $V_3 + V_4 \approx 2 \cdot 10^{-6}$ mol L⁻¹ s⁻¹ and $V_{\text{BS}} + V_3 + V_4 = 16 \cdot 10^{-6}$ mol L⁻¹ s⁻¹, which is noticeably lower than $V_{\text{TS}} = 28 \cdot 10^{-6}$ mol L⁻¹ s⁻¹. This is the socalled synergism of action of components of the amineepoxide-acid TS with an interesting mechanism. Synergism is convincingly demonstrated by curve 5: epoxide $(0.52 \text{ mol } L^{-1})$ was added to the oxidate (final solution) of the experiment (see Fig. 1, curve 4), and the O_2 uptake rate increased to almost the value of V_2 (oxidation rate of the TS).

The results of manometric experiments with three nitrogen bases, **3**, **7**, and **10**, are presented in Fig. 2. The both primary aromatic amines introduced into BS 1-2accelerate oxidation (see Fig. 2, curves *I* and *2*). The higher the concentration of amines, the lower the efficiency of the subsequent acceleration: plots *I* and *2* have a character of curves with saturation (at the limiting level). The oxidates of the experiments presented by curves *I* and *2* are red—cherry-colored. Pyridine (**10**) behaves in a different manner: there are no visual signs of its active participation in oxidation, since of the oxidates of the experiments presented by curve *3* are colorless and transparent. As the concentration of pyridine **10** increases, the oxidation rate



Fig. 2. Oxygen uptake rates (*V*) at $[1]_0 = 0.52 \text{ mol } L^{-1}$ depending on [7] at [2] = 0.034 mol L^{-1} (*I*), on [3] at [2] = 0.016 mol L^{-1} (*2*), and on [10] at [2] = 0.034 mol L^{-1} (*3*) and the dependences on [10] of the aldehyde accumulation rate [12] (*4*) and the residual [1] in the oxidates of experiments corresponding to curve *3* (*5*); [1]₀ = 0.52 mol L^{-1} , MeCN, 343 K.

109

Entry	Solvent	Reagent (C /mol L ⁻¹)			<i>V</i> •10 ⁶
		Epoxide	Acid	Amine	$/mol L^{-1} s^{-1}$
1	PhCl	1 (0.52)	2 (0.021)	7 (0.44)	2.0
2	PhCl	1 (0.52)	2 (0.021)	-(0)	1.3
3	$Bu^{t}OH-PhCl(9:1)$	1 (0.52)	2 (0.0055)	3 (0)	5.6
3'	The same	1 (0.52)	2 (0.0055)	3 (0.07)	10.0
4	*	1 (0)	2 (0.0055)	3 (0.07)	0.5
4′	*	1 (0.52)	2 (0.0055)	3 (0.07)	11.0
5	»	1 (0.52)	2 (0)	3 (0.07)	~0.1
5′	»	1 (0.52)	2 (0.0055)	3 (0.07)	11.0
6	AcOH(20%)-MeCN(80%)	1 (0.52)	AcOH (3.5)	-(0)	1.5
7	The same	1 (0.52)	AcOH (3.5)	5 (0.076)	5.0
8	»	1(0)	AcOH (3.5)	5 (0.074)	0.2
8'	»	1 (0.52)	AcOH (3.5)	5 (0.074)	4.5
9	AcOH(10%)-MeCN(90%)	1 (0)	AcOH (1.75)	3 (0.098)	~0.3
9′	The same	1 (0.52)	AcOH (1.75)	3 (0.098)	2.3
10	»	1 (0.52)	AcOH (1.75)	3 (0)	0.7
10'	»	1 (0.52)	AcOH (1.75)	3 (0.097)	3.0
11	MeCN	1 (0.52)	2 (0.016)	3 (0.11)	19.0
12	The same	1 (0.52)	2 (0.016)	-(0)	6.0
13	»	1(0)	2 (0.016)	3 (0.11)	1.3
13′	»	1 (0.52)	2 (0.016)	3 (0.11)	19.0
14	»	1 (0.52)	2 (0)	3 (0.11)	0.5
14′	»	1 (0.52)	2 (0.016)	3 (0.11)	18.0
15	»	8 (0.35)	2 (0.0114)	7 (0)	2.4
15´	»	8 (0.35)	2 (0.0114)	7 (0.1)	5.0
16	»	8 (0.33)	2 (0.0114)	7 (0.11)	4.6
17	»	8 (0)	2 (0.0118)	7 (0.114)	0.5
17′	»	8 (0.33)	2 (0.0118)	7 (0.114)	4.5
18	»	8 (0.34)	2 (0)	7 (0.12)	~1.0
18′	»	8 (0.34)	2 (0.0114)	7 (0.12)	4.3
19	»	9 (0.17)	2 (0.011)	7 (0)	11.0
<i>19′</i>	»	9 (0.17)	2 (0.011)	7 (0.104)	20.0
20	»	9 (0.17)	2 (0.0068)	7 (0)	7.5
20'	»	9 (0.17)	2 (0.0068)	7 (0.104)	12.1
21	»	9 (0.17)	2 (0)	7 (0.11)	0
21´	»	9 (0.17)	2 (0.0064)	7 (0.11)	10.0
22	»	9 (0.17)	2 (0.0068)	7 (0.11)	11.0

Table 1. Results of the preliminary study of the acceleration of binary systems (BS) epoxide—acid by amines at 343 K

and rate of aldehyde **12** accumulation (curves 3 and 4) decrease. The residual concentration of epoxide $[1]_t$ in the oxidates of the experiments presented by curve 3 increases with an increase in [10] (curve 5). Therefore, the consumption rate of 1 decreases with an increase in [10].

These data are well consistent with the results of experiments on the oxidation in the bubbling reactor of BS 1-2, TS 1-2-7, and BS 1-2 + 10 with the HPLC study of the accumulation of compounds 11 and 12 and consumption of compound 1 (Fig. 3).³ The consumption of compound 1 in the BS (curve *1*) is accompanied by the accumulation of relatively high concentration of 11 and 12 (curves *1'* and *1''*). For the oxidation of TS, the kinetics of consumption of 1 (curve 2, black points) do not differ from that for the BS (curve *1*, light points). However, in

this case, the accumulation rate of compound **11** two times decreases (*cf.* curves 1' and 2') and aldehyde **12** is not almost accumulated (curve 2''). The introduction of pyridine **10** in the BS inhibits both the consumption of compound **1** (curve 3) and accumulation of both aldehydes (curves 3' and 3'').

Based on the data in Figs 2 and 3, we can assume the nature of the effect of amines introduced into the BS. Additives of amines and model inert base **10** undoubtedly shift the acid—base equilibrium, decreasing the concentration of protonated epoxide (Scheme 1).

This shift is proved by a decrease in the oxidation rate (see Fig. 2, curve 3) and the rate of epoxide consumption (see Fig. 2, curve 5) with an increase in [10] and also by a decrease in the concentration of aldehyde 12 in the pres-



Fig. 3. Kinetic curves of consumption of epoxide 1 (*1*–3, circles) and accumulation of benzaldehyde 11 (*1'*–3', triangles) and aldehyde 12 (*1''–3''*, rhombi) in a MeCN solution, [1]₀ = $= 0.52 \text{ mol } L^{-1}$, [2] = $0.034 \text{ mol } L^{-1}$, 343 K: oxidation of BS 1–2, light points (*1*, *1'*, *1''*); oxidation of TS 1–2–7, [7] = $0.25 \text{ mol } L^{-1}$, black points (*2*, *2'*, *2''*); oxidation of the BS in the presence of pyridine 10, [10] = $0.41 \text{ mol } L^{-1}$, black—white points (*3*, *3'*, *3''*).

Scheme 1

SE is styrene epoxide, NB is nitrous base.

ence of all nitrogen bases tested by us (see Figs 2 and 3). The detailed mechanism of formation of aldehyde 12 in solutions of H-acids from compound 1 is unknown; however, the protonation of epoxide as a necessary prerequisite for the formation of aldehyde 12 is always postulated.⁶ Therefore, it is quite unexpected that aldehyde 12 is nearly completely absent from the oxidates of manometric experiments with all amines tested in this work. Pyridine 10 is a stronger base than compound 7, $pK_{PvH^+} = 5.21$, $pK_{7H^+} =$ = 4.62 (H₂O, 298 K).⁷ If the accumulation of aldehyde 12 at unchanged concentrations of compounds 1 and 2 would be determined by the protonated epoxide content only, pyridine 10 should more strongly suppress the accumulation of aldehyde 12. However, aldehyde 12 is nearly absent in all oxidates of experiments with amines (see Fig. 2, curves 1 and 2). In the case of pyridine 10, aldehyde 12 is accumulated in measurable amounts even at high [Py] (see Fig. 2, curve 4, cf. curves 2" and 3" in Fig. 3). The sharp decrease (by one-two orders of magnitude) in the concentration of aldehyde 12 in the presence of amines is explicitly caused not only by proton-acceptor properties of these bases. Possibly, the route of oxidation of TS 1-2-amine proceeds through the same intermediate compounds of particles that precede the formation of aldehyde 12. Possibly, amines themselves, regardless of their relation to oxidation, block the formation of aldehyde 12 interacting with particle-precursors of formation of aldehyde **12** and thus decreasing their concentration. The problem is new and interesting, and its study requires special efforts.

Ternary system 1–2-amine is complicated for investigation, and it is impossible to propose a specific mechanism for oxidation on the basis of the obtained results. Literature data cannot help: in a huge number of works on acid- and base-catalyzed transformations of epoxides, the authors operate only with concepts in the framework of heterolysis. In addition mixing of H-acid and base, as it was done in our work, seems unreasonable from the viewpoints of concepts on the mechanisms of reactions of epoxides and the practice of using epoxides, for example, via catalyzed solidification. A similar case was described earlier⁸: the acid-catalyzed oxidation of the BS and decomposition of hydroperoxide in the TS accelerated with an increase in the alcohol concentration in the solution accompanied by a decrease in the acidity. We believe that the interaction of positively charged protonated particles with neutral particles resulting in the formation of an intermediate complex that transforms via parallel heterolytic (A) and homolytic (B) routes (Scheme 2) can be accepted to be the basis of the scheme of the mechanism of oxidation of TS amine-epoxide-acid.







The inhibition ability of amines seems to be insignificant: strictly speaking, compound 7 is not inhibitor, unlike 3, but, as it is clear from the results of our work, the acceleration effect of these amines is comparable. A similar acceleration of BS oxidation involving phenols was found only in experiments with hydroquinone. Probably, the acceleration of oxidation of BS 1-2 is related to the oxidation of amines in TS amine-1-2. The following variants of the mechanism are possible:

(1) amines are oxidized with participation of the desired quasi-radical particle that appears in the BS;

(2) the oxidation of TS amine-1-acid proceeds *via* different mechanism that the oxidation of BS 1-acid;

(3) amines are oxidized by accumulated H_2O_2 .⁹

It is difficult to elucidate each contribution because of a complicated experiment: it is impossible to iodometrically monitor the hydrogen peroxide concentration in brightly colored oxidates of the TS. The study of the nature of colored products is promising: the color appears only in an oxygen atmosphere. The general conclusion of this and our previous works on the acid-catalyzed conversion of compound **1** is that these transformations are not incompletely heterolytic. Parallel routes with the formation of active intermediate particles that rapidly react with oxygen occurs against the background of the predominant heterolytic channel. The present work seems promising, in particular, for search for new TS in the respect of enlarging the topic we are interested in of the competition of heterolysis and homolysis¹⁰ using acid-catalyzed reactions of compound **1**. It should be mentioned that data on the reactions of salts of strong acids and organic bases with compound **1** are available.¹¹ However, the possibility of the radical route to occur is not reported.

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