Phenylmethylene as intermediate in acid-catalyzed oxidation of styrene epoxide

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The absorption spectrum of iminium ylide ($\lambda_{max} = 450$ nm) has been registered under the conditions of acid-catalyzed consumption of styrene epoxide under the influence of *p*-toluenesulfonic acid (MeCN, Bu^tOH (90 vol.%) + chlorobenzene (10 vol.%), 343 K) in the presence of pyridine. The spectrum coincides with the spectrum of the ylide product of the interaction of pyridine with phenylcarbene of phenylmethylene formed in the conventional flash-photolytic preparation of carbene from diazo derivative. The result confirms the earlier assumption on the formation of the particles of carbene nature reacting with oxygen in the epoxy-acid system. In the absence of O₂ these particles destruct introduced hydroperoxides. The spectra of corresponding carbonyl oxide ($\lambda_{max} \approx 408$, 400 nm) in the presence and absence of pyridine were recorded in acetonitrile.

Key words: styrene epoxide, *p*-toluenesulfonic acid, acetonitrile, *tert*-butanol, pyridine, ylide, phenylcarbene of phenylmethylene, molecular oxygen, carbonyl oxide of phenylmethylene.

Acid-catalyzed process of styrene epoxide (1) consumption in polar media (Bu^tOH, MeCN) is the result of competition between two proceeding parallel routes: dominant heterolytic process (~95%) and homolytic (~4–5%) process, which is able to produce active intermediates reacting with O₂ forming benzaldehyde, and in an Ar atmosphere destroy hydroperoxides (ROOH) at 343 K.^{1,2} High stability of pure epoxide 1 to the radicalchain oxidation (initiator, 413 K)³ is in marked contrast to its lability in respect to oxygen in the presence of acid at 343 K.^{2,4}

Acid-catalyzed conversions of epoxides, in particular compound 1, in polar media were considered for a long time traditionally as purely heterolytic reactions.⁵ It has been found in detailed kinetic study of mild acid-catalyzed oxidation of epoxide 1 in a mixed solvent BUC (90 vol.% of Bu^tOH and 10 vol.% of chlorobenzene) that heterolytic and homolytic routes of the consumption of 1 in the presence of *p*-toluenesulfonic acid (2) are clearly symbatic.⁴



The study of the triple system (ROOH-1-2) led to the variant of stepwise conversion of epoxide with the formation of triplet carbene as intermediate: protolysis of $1 \rightarrow$ carbocation \rightarrow carbene—phenylmethylene (3) \rightarrow \rightarrow uptake of oxygen.¹ Identity of the reaction orders of the 1 consumption for epoxide and acid in acid-catalyzed process and uptake of O₂ in this process, selective formation of C₆H₅CHO, strong agreement of retardation of homolytic and heterolytic conversion of epoxide 1 by catalytic amounts of halides,⁵ are the indices that confirm this Scheme.

However, the possibility of carbenes appearance as the result of chemical reactions in these systems seemed theoretically improbable. Calculations of the formation heats of the compound **3** in the gas phase performed by various methods showed a significant limitation of the thermochemical process.^{6,7}

Experimental

Absorption spectra of studied solutions were registered at 298 and 343 K using fiber optic spectrometer HR-2000 (Ocean Optics). Integration time was set to 5 ms. The sensitivity of spectrometer at studied wavelength was not less than 0.002. OOI Base32 software was used for spectra processing. Working concentrations of the reagents ([1]₀ > [4] >> [2]) were selected on the basis of experimental data obtained previously.^{1–5} Investigated solutions in the sealed quartz cuvettes (l = 1 cm) were flushed with dry argon for 20 min or, if required, by O₂. The heating of cuvettes (10 min) to the

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reaction temperature and temperature maintaining was performed with the help of water thermostate. The registration of spectra was carried out according to time plan. The oxidation rates (V_{O_2}) were measured volumetrically according to earlier described procedure.⁵ Initial and final content of epoxide 1, and if required of benzaldehyde and phenylacetyl aldehyde (products of homolytic and heterolytic conversion, respectively) were determined by HPLC.⁴

The quality of reagents was controlled by HPLC, GC, and also kinetically by the reproduction of earlier obtained data for the oxidation in binary system (BS) 1–2. Epoxide 1 and pyridine (4) were purified by vacuum distillation in Ar atmosphere. Chlorobenzene was treated several time with H_2SO_4 , then washed with water, dried over CaCl₂, and distilled. MeCN (Acros Organics, HPLC UV), Bu^tOH (Reachim, analytical grade), *p*-toluenesulfonic acid monohydrate (Reachim, pure) were used as received.

Results and Discussion

The reactions of electrophylic carbenes with compounds containing C=N bond with the formation of iminium ylides as labile intermediates (Scheme 1) are generally used to identify carbenes and to study their reactivity. High rate of carbenes interaction with compound **4** is the basis of technique of the pyridine sampling. For example, $k_4^{298\text{K}}$ for singlet state and triplet state⁸⁻¹⁰ of compound **3** consists of $1 \cdot 10^9 \text{ L} \text{ mol}^{-1}\text{s}^{-1}$ and $9.3 \cdot 10^6 \text{ L} \text{ mol}^{-1}\text{s}^{-1}$, respectively.





Iminium ylide (5) is a product of the reaction of pyridine with carbene obtained from diazo compounds of corresponding structure using vacuum flash-thermolysis (FVT), laser flash-photolysis (LFP) in solution or solid matrix. The presence of this intermediate is registered in UV or visible range of spectrum using high-speed spectroscopy (up to 400 ns due to small lifetime of ylides) at room temperature in anaerobic conditions.^{8,10}

To detect carbene intermediate in the solutions of epoxide 1 in the presence of compound 2 the pyridine was also used as a trap. In accordance with the literature data,⁸⁻¹⁰ in the conditions of catalyzed consumption of the epoxide 1 (343 K) in epoxy-acid system (1–2) in polar media (MeCN or BUC), and in Ar atmosphere, the formation of compound 3 in the presence of 4 should be manifested in the characteristic absorption band of pyridinium ylide 5 (see Scheme 1) in the spectrum.

Acid-catalyzed conversion (net consumption) of epoxide 1 in Ar and O_2 atmospheres is undergoing practically with a constant rate, at time zero order, almost to complete disappearance of epoxide 1.^{4,11} Thus, the kinetic data for epoxide 1 consumption and oxygen uptake allow us to suggest constant rate of the formation of active particles for a considerable time period and minimum negative effect from the presence of the heterolysis products of epoxide 1 under the conditions of system 1–2 (see Ref. 1). Also as the result of the all above mentioned facts the accumulation of steady-state concentration of ylide is sufficient for the observation.

The investigation of absorption spectra of the solutions of BS 1-2 in the presence of pyridine 4 at 343 K in Ar atmosphere in BUC (Fig. 1, *a*, spectra 1-9 and 1'-4') and in MeCN (Fig. 1, *b*, spectra 1''-7'') has shown that



Fig. 1. Absorption spectra of BS 1–2 in the presence of **4** in solutions (343 K, Ar): *a* is BUC (1–9) ([1]₀ = 1.044, [1]_{KOH} = = 0.39, [2] = 0.0932, [**4**] = 0.4 mol L⁻¹) at reaction time 180 (1), 300 (2), 480 (3), 600 (4), 780 (5), 900 (6), 1200 (7), 1800 (8), 2400 s (9). (1'-4') is BUC ([1]₀ = 1.044, [2] = 0.0233, [**4**] = 0.112 mol L⁻¹) at reaction time 180 (1'), 300 (2'), 1800 (3'), 3600 s (4'); *b* is MeCN (1–6) at [**2**] = 0.034, [**4**] = 0.2 mol L⁻¹; (1'-6') at [**1**]₀ = 0.52, [**4**] = 0.2 mol L⁻¹; (1''-7') at [**1**]₀ = 0.52, [**1**]_{KOH} = 0.43, [**2**] = 0.034, [**4**] = 0.2 mol L⁻¹. Reaction time (s): 600 (1, 1', 1''), 1200 (2, 2', 2''), 1800 (3, 3', 3''), 2400 (4, 4', 4''), 3000 (5, 5', 5''), 3600 (6, 6', 6''), 4200 (7'').

at $[4] \ge 0.2 \text{ mol } \text{L}^{-1}$ stable increase of the optical density in the range of 430–480 nm corresponding to absorption of phenyl-substituted ylides is registered in time.⁸ This has not been observed (see Fig. 1, *b*, spectra *1*–6 and *1'*–6') in the spectra of pairs **2**–4 and **1**–4 in the absence of one of the components of binary epoxy-acid system, particularly epoxide **1**.

The choice of working concentration of pyridine in solutions of MeCN and BUC allowed to select the compromise conditions of experiments: comparability of rates of consumption of the active particles in competing reactions, also with the trap 4, and acceptable threefold decrease in the acidity of the solution in the presence of the base 4. Characteristic bands of ylides (430–480 nm) do not appear in the absorption spectra of BS 1–2 in O₂ atmosphere in the presence of compound 4 (Fig. 2, *a*, spectra 1-8 and Fig. 3, *a*, spectra 1-8). This fact is due to fast reaction of the carbene with oxygen. Triplet arylcarbene intermediates react with O₂ by several or-



Fig. 2. Absorption spectra of BS 1–2, MeCN, 343 K: *a* is in the presence of **4**, $[\mathbf{1}]_0 = 0.52$, $[\mathbf{2}] = 0.034$, $[\mathbf{4}] = 0.2 \text{ mol } L^{-1}$, O₂, at reaction time 300 (*1*), 600 (*2*), 900 (*3*), 1500 (*4*), 2400 (*5*), 3000 (*6*), 3600 (*7*), 4200 s (*8*). $[\mathbf{1}]_{\text{KOH}} = 0.42 \text{ mol } L^{-1}$; *b*, at $[\mathbf{4}] = 0$, $[\mathbf{1}]_0 = 0.52$, $[\mathbf{2}] = 0.0106 \text{ mol } L^{-1}$, Ar, at reaction time 300 (*1*), 480 (*2*), 600 (*3*), 900 (*4*), 1200 (*5*), 1800 (*6*), 2400 (*7*), 3000 (*8*), 3600 s (*9*).



Fig. 3. Absorption spectra in BUC at 343 K: *a* is BS **1**–**2** in the presence of **4** ($[1]_0 = 1.044$, [2] = 0.0932, $[4] = 0.4 \text{ mol } L^{-1}$), O₂, at reaction time 180 (*1*), 300 (*2*), 480 (*3*), 600 (*4*), 780 (*5*), 900 (*6*), 1200 (*7*), 1800 s (*8*), $[1]_{\text{KOH}} = 0.388 \text{ mol } L^{-1}$; *b* is for compound **5**, as the result of subtraction of absorption spectra of system BS **1**–**2** + **4** in Ar and O₂ atmospheres, at reaction time 600 (*1*), 780 (*2*), 900 (*3*), 1200 (*4*), 1800 s (*5*).

ders of magnitude faster than with pyridine (4): for example, for diphenylmethylene in MeCN $k_4^{298K} =$ = 2.8–4.2 · 10⁵ L mol⁻¹ s⁻¹ (see Ref. 12), and $k_{O_2}^{298K} =$ = 5 · 10⁹ L mol⁻¹ s⁻¹ (LFP).¹³ For the same reason hydroperoxides introduced into BS 1–2 are not destroyed in the O₂ atmosphere.¹

Phenyl-substituted pyridinium ylides have weak absorption bands.^{9,10} The initial view of the spectra obtained in BS is complicated by the background absorption associated with the accumulation of epoxide 1 conversion products (see Figs 1 and 2). The background removing was performed in two ways. In the first case, from the optical density of the absorption spectra of BS-4 system in Ar atmosphere the values of absorption obtained for this system at similar reaction conversion in the O₂ atmosphere were subtracted (Fig. 4, *a*, spectra 1-7 and Fig. 3, *b*, spectra 1-5). In the second case, the values of absorption measured in the absence of trap 4





Fig. 4. Absorption spectra of compound **5** in MeCN (343 K), obtained by subtraction of the absorption values of the system using first and second procedures: *a* is BS **1**–**2** + **4** in Ar and O₂ atmospheres ([**1**]₀ = 0.52, [**2**] = 0.034, [**4**] = 0.2 mol L⁻¹) at reaction time 600–600 (*1*), 1200–900 (*2*), 1800–1500 (*3*), 2400–2400 (*4*), 3000–3000 (*5*), 3600–3600 (*6*), 4200–4200 s (*7*); *b* is BS **1**–**2** + **4** ([**1**]₀ = 0.52, [**2**] = 0.034, [**4**] = 0.2 mol L⁻¹) and BS **1**–**2** ([**1**]₀ = 0.52, [**2**] = 0.0106 mol L⁻¹, Ar) at reaction time 600 (*1*), 1200 (*2*), 1800 (*3*), 2400 (*4*), 3000 (*5*), 3600 s (*6*).

(in Ar atmosphere) at similar rate of generation of reactive intermediates were subtracted (see Fig. 4, *b*). Obtained in these ways difference spectra for BUC and MeCN solutions (343 K) contain well pronounced band with a maximum at 440—450 nm, characteristic of the reaction product of active intermediate with pyridine **4** (see Figs 3 and 4). The amplitudes of noise in this case are many times smaller than amplitudes of bands in the obtained spectra.

The nature of the spectra obtained by subtracting using the first method (see Fig. 3, *b* and Fig. 4, *a*) both in MeCN and in BUC shows that the constant concentration of the new compound is established in the system for the time ≤ 10 min. This observation is consistent with the zero order consumption of epoxide 1 and constant rate of the O₂ uptake.¹¹ The peculiarity of the solvent used is manifested by a small hypsochromic shift from 450 to 440 nm in aprotic MeCN with increasing of time of spectra recording (see Fig. 4, *a*). In alcoholic BUC medium (λ_{max} = 450 nm) that shift is not detected even at three times higher degree of the epoxide decomposition (see Fig. 3, *b*).

An increase in the concentration of pyridine (4) in MeCN decreases the O_2 uptake rate by BS solutions 1-2in the oxygen atmosphere.¹⁴ The uptake rate is indicator of the active particles generation. The presence of compounds 1, 2, and 4 in solutions should lead to several equilibrium acid-base processes with the participation of these compounds.14 Complete neutralization of compound 2 by the base does not take place here (see Fig. 1, b, spectra 1'-6' and 1''-7''). In order to calculate reaction rate in this experiment the dependence of V_{O_2} on the concentration of compound 4 from the Ref. 14, obtained in similar condition and with the same batches of reagents, was used. Input of 0.2 mol L^{-1} of compound 4, at $[\mathbf{2}] = 0.034 \text{ mol } \mathrm{L}^{-1}$, decreases the value of V_{O_2} by 3.1 times, from $16.0 \cdot 10^{-6}$ mol L⁻¹ s⁻¹ to $5.2 \cdot 10^{-6}$ mol L⁻¹ s⁻¹. Consequently, taking into account equality of the rates of net epoxide 1 consumption in argon and oxygen atmospheres,^{4,11} this fact provides for the decrease of the intermediate generation in Ar atmosphere by 3.1 times. Then taking into account zero order of oxidation reaction for epoxide and first reaction order for acid⁴ the spectrum for control subtraction by second method was registered in three times smaller content of compound 2 $(0.0106 \text{ mol } \text{L}^{-1})$. This procedure (see Fig. 4, b) provides for the comparison at lower reaction conversion. However, the maxima of resulting spectra of compound 4 reaction products with identified carbene intermediate, obtained by the second method (Ar atmosphere) are close



Fig. 5. Comparison of the absorption spectra of compound 5 (1, 2) in MeCN at 343 K, obtained by subtraction of the absorption values using first and second procedures (reaction time 600 s) for systems: BS 1-2+4 ([1]₀ = 0.52, [2] = 0.034, [4] = 0.2 mol L⁻¹) in Ar and O₂ atmospheres (1), and also BS 1-2+4 ([1]₀ = 0.52, [2] = 0.034, [4] = 0.2 mol L⁻¹) and BS (1-2) ([1]₀ = 0.52, [2] = 0.0106 mol L⁻¹) in Ar atmosphere (2).





to the estimate data obtained using of the first method (Ar, O_2 atmospheres), 450 and 445 nm, respectively (see Fig. 5, spectra 1-2).

The values of absorption maxima in polar media obtained in two ways of subtraction are close to the values for compound 5 obtained *via* laser flash-photolysis at room temperature: 460 nm (*n*-pentane),¹⁰ 474 nm (freon-113),⁹ 450 nm.⁸. A small shift of maximum in our conditions is explained by hypsochromic shift in the polar solvent.

Carbonyl oxides (CO) (Scheme 2) are primary products of the oxidation reaction of triplet aromatic carbenes in oxygen atmosphere.^{13,15} Characteristic spectra of CO, labile intermediates of the oxidation reaction, are known for many cases in MeCN.^{15–18} Thus, for the carbonyl oxide of phenylmethylene (6) λ_{max} consists of 407±20 nm.^{15,17,18}

The spectra of the system $1-2 + 4 + O_2$ in MeCN, obtained by the first method of subtraction of the background absorption, but in the reverse order, *i.e.* $A_{O_2}-A_{Ar}$, exhibit a weak absorption band of the reaction intermediate in the range of 390–420 nm, which at the average maximum (408 nm) corresponds to the absorption of compound **6** (Fig. 6, *a*, spectra 1–6). As in the case of compound **5**, the time variation of the intensity of the absorption band is small. It allows us to suggest that in the system (at $[1]_{\text{final}} > 0$) the stationary concentration of compound **6** is established. In the absence of pyridine, similarly, in the same area of 390– 420 nm the similar band with close peak at 400–403 nm appears in the spectrum of a binary system **1–2** in oxygen atmosphere (Fig. 6, *b*). The data are not sufficient to calculate the value of ε_{ROO} (molar extinction coefficient), but a rough quantitative estimate based on the values of ε_{ROO} for aryl-substituted CO published in Ref. 16 (($\varepsilon_{\text{ROO}} = 1400\pm500 \text{ L} \text{ mol}^{-1}\text{ cm}^{-1}$) is possible. Supposing that

$\Delta A_{\lambda \max} = \varepsilon \cdot l \cdot m,$

where ΔA_{λ} is the change of absorption at λ_{max} ; *l* is the cuvette length, cm; *m* is the concentration of determined intermediate, mol L⁻¹. For values of $\Delta A_{\lambda max}^{+Py} = 0.01$ (see Fig. 6, *a*), $\Delta A_{\lambda max} = 0.03$ (see Fig. 6, *b*), for systems (1–2) + + **4** + O₂ and (1–2) + O₂ in MeCN we obtain the values of $m = 7.1 \cdot 10^{-6}$ and $2.1 \cdot 10^{-5}$ mol L⁻¹, respectively. The formation of compound **6** in BS 1–2 + O₂ explains fast oxidation of introduced into the system readily oxidizable



Fig. 6. Absorption spectra of compound **6** in MeCN at 343 K: *a* is difference of optical densities of BS 1-2 + 4 in Ar and O₂ atmospheres ([1]₀ = 0.52, [2] = 0.034, [4] = 0.2 mol L⁻¹) at reaction time 1200–900 (*I*), 1800–1500 (*2*), 2400–2400 (*3*), 3000–3000 (*4*), 3600–3600 (*5*), 4200–4200 s (*6*); *b* – difference of optical densities of BS 1-2 in Ar and O₂ atmospheres ([1]₀ = 0.52, [2] = 0.015 mol L⁻¹) at reaction time 600 (*I*), 900 (*2*), 1200 (*3*), 1800 s (*4*).

substrates, such as styrene or isopropanol.¹⁹

Thus, the data of presented spectral study of BS 1-2in the presence and absence of the chemical traps (pyridine and oxygen) indicate the formation of carbene and carbonyl oxide in the system. Pyridinium ylide of phenylmethylene is detected in the system (1-2) + 4 in Ar atmosphere, and carbonyl oxide of phenylmethylene is detected in oxygen atmosphere. This confirms the earlier assumption¹ on the oxidation of binary epoxy-acid system without the formation of peroxide radicals.

References

- 1. L. V. Petrov, V. M. Solyanikov, *Petroleum Chem. (Engl. Transl.)*, 2005, **45**, 202 [*Neftekhim.*, 2005, **45**, 225].
- L. V. Petrov, V. M. Solyanikov, *Petroleum Chem. (Engl. Transl.)*, 2010, **50**, 437 [*Neftekhim.*, 2010, **50**, 447].
- L. V. Petrov, B. L. Psikha, V. M. Solyanikov, *Petroleum Chem.* (*Engl. Transl.*), 2009, **49**, 245 [*Neftekhim.*, 2009, **49**, 263].
- L. V. Petrov, V. M. Solyanikov, Petroleum Chem. (Engl. Transl.), 1999, 39, 89 [Neftekhim., 1999, 39, 107].
- L. V. Petrov, V. M. Solyanikov, *Petroleum Chem. (Engl. Transl.)*, 2012, **52**, 327 [*Neftekhim.*, 2012, **52**, 362].
- 6. Yu. D. Orlov, Yu. A. Lebedev, L. G. Menchikov, O. M. Nefedov, *Russ. Chem. Bull. (Engl. Transl.)*, 1997, 46, 52 [*Izv. Akad. Nauk, Ser. Khim.*, 1997, 57].
- 7. T. L. Nguyen, G.-S. Khim, A. M. Mebel, M. T. Nguen, *Chem. Phys. Lett.*, 2001, **349**, 571.

- A. F. Khlebnikov, M. S. Novikov, R. R. Kostikov, Russ. Chem. Rev. (Engl. Transl.), 2005, 74, 171 [Usp. Khim., 2005, 74, 183].
- 9. A. Admasu, A. D. Gudmundsdottir, M. S. Platz, *J. Phys. Chem. A*, 1997, **101**, 3832.
- A. Admasu, M. S. Platz, A. Marcinek, J. Michalak, A. D. Gudmundsdottir, J. Gebicki, J. Phys. Org. Chem., 1997, 10, 207.
- L. V. Petrov, V. M. Solyanikov, Petroleum Chem. (Engl. Transl.), 2013, 53, 326 [Neftekhim., 2013, 53, 369].
- 12. M. B. Jones, M. S. Platz, Tetrahedron Lett., 1990, 31, 953.
- J. C. Scaiano, W. G. McGimpsey, H. L. Casal, J. Org. Chem., 1989, 54, 1612.
- L. V. Petrov, V. M. Solyanikov, Russ. Chem. Bull. (Int. Ed.), 2015, 64, 107 [Izv. Akad. Nauk, Ser. Khim., 2015, 107].
- 15. W. H. Bunnelle, Chem. Rev., 1991, 91, 335.
- A. M. Nazarov, E. M. Chainikova, I. A. Kalinichenko, S. L. Hursan, R. L. Safiullin, V. D. Komissarov, *Russ. Chem. Bull.* (*Engl. Transl.*), 1999, 48, 672 [*Izv. Akad. Nauk, Ser. Khim.*, 1999, 677].
- D. Cremer, T. Schmidt, W. Sander, P. Bischop, J. Org. Chem., 1989, 54, 2515.
- I. A. Kalinichenko, PhD Thesis (Chem.), Institute of Organic Chemistry of Ufa Scientific Center of Russian Academy of Sciences, Ufa, 1999, 161 pp. (in Russian).
- L. V. Petrov, V. M. Solyanikov, *Petroleum Chem. (Engl. Transl.)*, 1998, 38, 117 [*Neftekhim.*, 1998, 38, 128].

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