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Dyes and Pigments 65 (2005) 83–87

DYES and PIGMENTS

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A kinetic study on decomposition of 2,2′-(3″-nitrophenylsulfonyl) ethyl ether

Wu Zuwang[a,*,1], Dong Zhentang[a], Chen Zhengxu[b]

[a] *State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, China*
[b] *Dankong Industrial and Trade Co. Ltd., Taizhou 318000, China*

Received 15 February 2004; received in revised form 14 May 2004; accepted 28 June 2004
Available online 15 September 2004

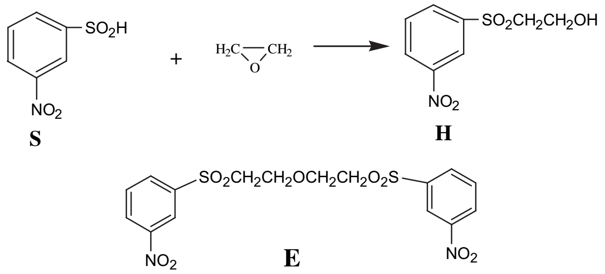
Abstract

The mechanism of decomposition of 2,2′-(3″-nitrophenyl) ethyl ether in an alkaline medium had been studied. It consists of two consecutive reversible reactions: (1) hydrolysis of the ether to 3-vinyl-sulfonyl nitrobenzene and 3-(β-hydroxy-ethylsulfonyl) nitrobenzene, (2) hydrolysis of 3-vinyl-sulfonyl nitrobenzene to 3-(β-hydroxy-ethylsulfonyl) nitrobenzene. The kinetic constants of these reversible reactions are given; the optimum hydrolysis condition was applied in industrial production.

Keywords: Reactive mechanism; 2,2′-Bi-(3″-nitrophenylsulfonyl) ethyl ether; 3-(β-Hydroxy-ethylsulfonyl) nitrobenzene; Kinetic constants

3-(Sulfato-ethylsulfonyl) aniline is a major intermediate for reactive dyes. It is prepared by chlorosulfonation of nitrobenzene, reduction with sodium sulfite, introducing the hydroxy-ethyl group with ethylene oxide, and esterification with sulfuric acid [1–7].

During oxy-ethylation of 3-nitro-benzene sulfinic acid (S) with ethylene oxide, 3-(β-hydroxy-ethylsulfonyl) nitrobenzene (H) formed and 2,2′-(3″-nitrobenzenesulfonyl) ethyl ether (E) was one of the main by-products in the reaction.



The formation of compound E is unavoidable, even when the reaction is carried out in a weakly alkaline medium. Hydrolysis of E is necessary both for improving the quality of the product and reducing the cost. The optimum hydrolysis conditions were studied [8], and the decomposition mechanism was investigated kinetically.

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* Corresponding author. Tel.: +86 411 8993811; fax: +86 411 3693296.
E-mail address: zuwangwu@dlut.edu.cn (W. Zuwang).

[1] Wu Zuwang is Professor of Dyestuff Chemistry and Fellow of Society of Dyers and Colorists, U.K.

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doi:10.1016/j.dyepig.2004.06.024

1. Experimental

1.1. *Purification of 3-(β-hydroxy-ethylsulfonyl)-nitrobenzene (H)*

3-(β-Hydroxy-ethylsulfonyl)-nitrobenzene was re-crystallized in methanol, a white crystal with M.P. 78.04–81.77 °C (DSC) and a purity of 98.99% was obtained. API-ES (Positive model) MS: MW 231 ($M + Na^+$: 254, $2M + Na^+$: 485),^1H NMR (DMSO-d_6): H_2 (8.64 ppm, d), H_4 (8.55 ppm, multi), H_5 (7.9 ppm, tetra), H_6 (8.35 ppm, tetra), SCH_2 (3.61 ppm, triple, 2H), OCH_2 (3.78 ppm, triple, 2H), OH (4.90 ppm).

1.2. *Preparation of 3-vinylsulfonyl-nitrobenzene (V)*

0.66 mol 104.5% oleum was added into a 150 mL beaker. At 20 °C, 0.13 mol H was slowly added, raised the temperature to 40 °C and kept for 3 h. When the reaction was complete, the reactant was slowly poured into 170 g of ice water. Added 30% NaOH to the suspension until the pH of the reaction medium changed to 12–13. The precipitate was filtered and washed with distilled water. The crude V with 97% yield was obtained. On re-crystallization in acetonitrile, a white crystal with purity of 97.65% of V was obtained. API-ES MS (Positive model): MW 213;^1H NMR: H_2 (8.58, d), H_3 (8.32, m), H_5 (7.97, tet), H_6 (8.57, m), CH= (7.26, tri), $=CH_2$ (6.36, d; 6.50, d).

1.3. *The preparation of 2,2′-(3″-nitrophenyl)-ethyl ether (E)*

Thirty grams of V and 150 ml 5% NaOH were added into a 250 mL three-necked flask equipped with a thermometer and a mechanical stirrer. This was heated to 75 °C and this temperature was maintained for 5 h. The precipitate was filtered off, 21.4 g of E was obtained after drying. On re-crystallization in acetonitrile, a light yellow powder with 98.91% purity (by HPLC) of E was obtained. M.P. 141.4–143.8 °C (DSC); MS: MW 444 ($M + Na^+$: 465, API-ES Positive);^1H NMR: H_2 (8.51, d), H_3 (8.22, m), H_5 (7.90, tet), H_6 (8.53, m), SCH_2 (3.54, tri), OCH_2 (3.60, tri)

1.4. *Determination the hydrolysis kinetic coefficient of E*

A 1000 mL three-necked flask equipped with a thermometer, a mechanical stirrer and a reflux condenser was placed in a thermostat bath, 0.005 mol of purified E in 250 mL acetonitrile was added into the flask, heated to a certain temperature. Meanwhile, 250 mL of 0.2 M Na_2CO_3 being pre-heated to the same temperature was rapidly poured into the flask. At certain intervals, 2 mL reactant samples were drawn and were diluted to 10 mL with a solution (acetonitrile:water:acetic acid = 50:45:5) to stop the reaction and were determined by HPLC.

1.5. *Determination of the hydrolysis kinetic coefficient of V*

E was replaced by 0.01 mol of purified V, and the same procedure as described in Section 1.4 was followed.

The standard curve of the above compounds gave linear relationships between the concentrations of $1–5 \times 10^{-3}$ M and their peak areas, the linear relative coefficients (R^2) were 0.9995, 0.9994 and 0.9884 for H, V and E, respectively.

1.6. *Analysis and analytical instruments*

HPLC: LDC/Milton Roy HPLC meter; 20 cm ODS 18 Column; eluent: acetonitrile:water = 50:50; current velocity: 1 mL/min; inspective wavelength: 254 nm. MS spectra: HP1000 HPLC-MS meter by API-ES method. ^1H NMR: Varian INOVA 400.

2. Results and discussion

In 1–3% sodium carbonate solution, E was completely decomposed to H at boiling temperature with a yield of 96%, no intermediate was found and only less than 2% of E remained at the end of hydrolysis. The regenerated E of high quality could be directly hydrogenated to prepare 3-hydroxy-ethylsulfonyl-aniline. The intermediate V could not be detected when hydrolysis was carried out at boiling temperature. The phenomena implied that the reaction was carried out in two steps. Firstly, E was hydrolyzed to V and H, and secondly, water was added to V to form H again. There were two reversible reactions during hydrolysis, and could be proved kinetically.

The intermediate V could be captured if hydrolysis was carried out at a lower temperature (Fig. 1).

The kinetic study data of hydrolysis of E at 40 °C in a buffer of pH 12.04 are given in Table 1 and the curve of reactant concentration–reaction time is shown in Fig. 2.

A typical consecutive reaction was found in Fig. 2, the concentration of E was reduced and the concentration of H increased with the reaction time, the concentration of intermediate V was increased and reached to a maximum concentration, then decreased as the reaction time went on. It seemed more likely that the reaction consisted of two series of parallel reactions, reactions (1) and (2). 2,2′-(3″-Nitrobenzenesulfonyl) ethyl ether (E) was hydrolyzed to 3-vinylsulfonyl-nitro-benzene (V) and 3-(β-hydroxy-ethylsulfonyl) nitro-benzene (H) at the

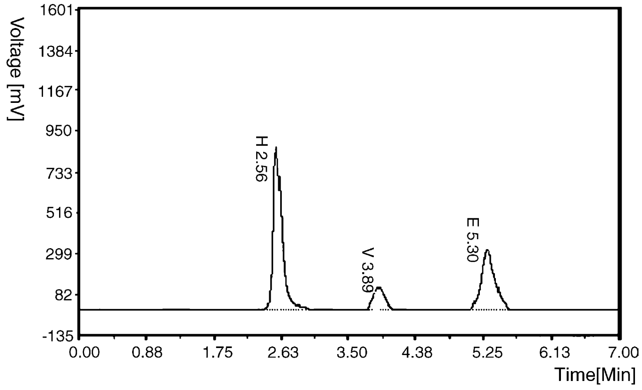


Fig. 1. The HPLC spectrum of hydrolysis of E at 40 °C (120 min).

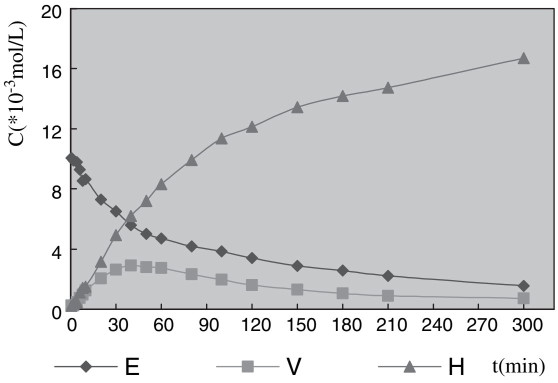
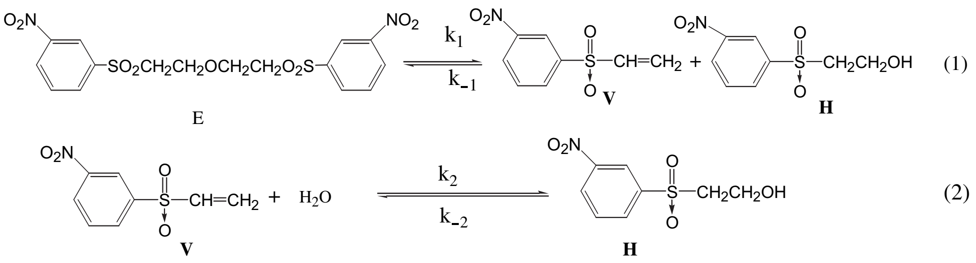


Fig. 2. C–t curve of hydrolysis of E at 40 °C.

first stage and the formed intermediate V was hydrated to H simultaneously.



For verification of the above hypothesis, compound V was applied as an initial compound and hydrolyzed with the same condition; the concentration–reaction time curve is shown in Fig. 3. Similar shape of the curves revealed that the reaction also consisted of by two series of parallel reactions, i.e., reactions (2) and (1), but only the intermediate compound is E.

The kinetic constants of the above reactions are given in Table 1.

The kinetic constants of reactions for hydrolysis of E and V are very similar. The pseudo-first order constants k_1 and k_2 are in the same order of 10^{-2}, which meant that E is decomposed to corresponding V and H; and V hydrolyzes to H, the similar reaction rate constants calculated at 40 °C, in a pH 12 buffer. The k_{-2} was two orders in magnitude less than k_1 and k_2. This indicated that dehydration of H to form V was much slower than hydrolysis of E and V. Only some amount of V was present at the initial stage of hydrolysis of E. When the concentration of V began accumulating at the initial stage, then hydrolysis of V was accelerated as the concentration of V increased, a maximum concentration of V was observed, and the concentration of V tended to become lower and lower as the reaction time went on.

Determination of the kinetic constants at 40 °C, 50 °C and 60 °C, the average apparent activation energies were calculated by Arrhenius equation (Table 2).

Average apparent activation energies of hydrolysis of E: $E_1 = 111.42$ kJ/mol;
Apparent activation energies of addition of water for V and H: $E_{-1} = 57.72$ kJ/mol;
Apparent activation energies of hydrolysis of V: $E_2 = 97.23$ kJ/mol;
Apparent activation energies of dehydration of H: $E_{-2} = 79.16$ kJ/mol.

The apparent activation energy of decomposition reaction of E was the utmost one in the reaction system (111.42 kJ/mol). This meant that the decomposition of E was very sensitive to temperature, but the reverse

Table 1
The kinetic constants of reactions (1) and (2) at 40 °C

Calculated	k_1 (min^{-1})	k_{-1} (L/mol min)	k_2 (min^{-1})	k_{-2} (min^{-1})
From hydrolysis of E	1.74×10^{-2}	2.09	2.09×10^{-2}	3.74×10^{-4}
From hydrolysis of V	1.95×10^{-2}	2.37	2.14×10^{-2}	2.74×10^{-4}

reaction, V and H to form E was of the least insensitive one; the apparent activation energy was 57.72 kJ/mol. The hydrolysis of E carried out at high temperature would be more favorable. The average apparent activation energies of hydrolysis of V (E_2) are much smaller than that of E_1. This could explain why the intermediate V could not be detected when hydrolysis was conducted at higher temperatures.

The mechanism of decomposition of E is elucidated as such: the withdrawing effect of the nitro group increases the reactivity of the hydrogen atom on the α carbon atom adjacent to the sulfonyl group, so E is easily hydrolyzed to V and H, and V is hydrolyzed in alkaline solution to form H.

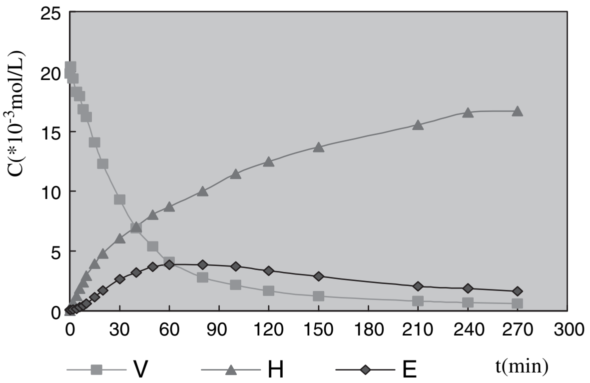
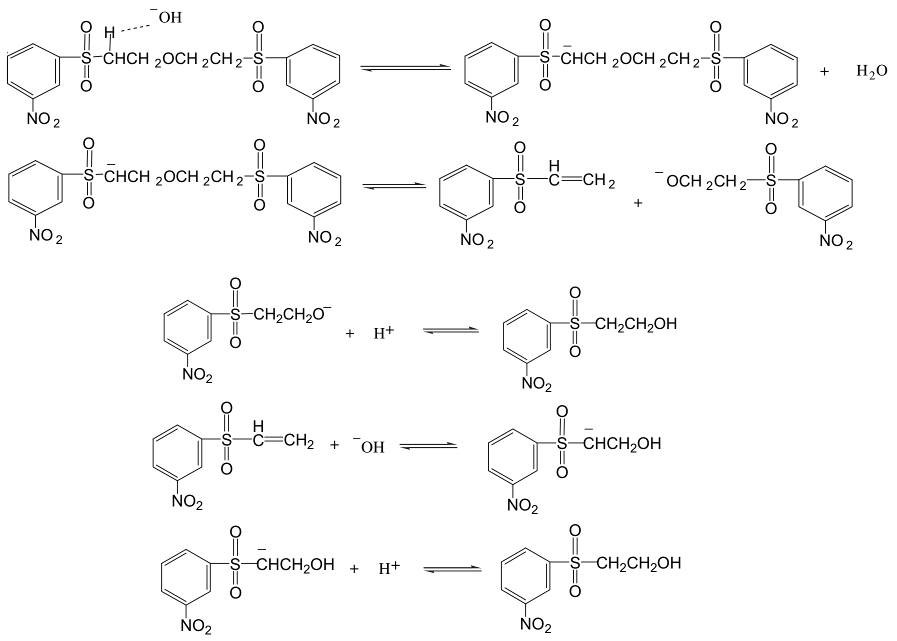


Fig. 3. C–t curve of hydrolysis of V at 40 °C.



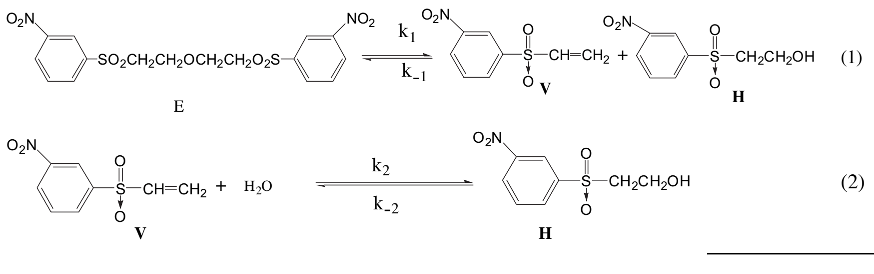
3. Conclusion

1. The decomposition of E consists of two consecutive reversible reactions: (1) hydrolysis of (E) and (2) hydrolysis of 3-vinylsulfonyl-nitrobenzene (V):

Table 2

The kinetic constants at different temperatures

	k_1 (min^{-1})	k_{-1} (L/mol min)	k_2 (min^{-1})	k_{-2} (min^{-1})
40 °C	1.76×10^{-2}	2.15	2.12×10^{-2}	3.37×10^{-4}
50 °C	6.73×10^{-2}	4.48	7.02×10^{-2}	7.93×10^{-4}
60 °C	2.30×10^{-1}	8.16	2.00×10^{-1}	2.08×10^{-3}



2. The kinetic constants of the above reactions were determined by HPLC in a pH 12 buffer. The pseudo-first order hydrolysis constants of 2,2′-(3″-nitrobenzenesulfonyl) ethyl ether and 3-vinylsulfonyl-nitrobenzene k_1 and k_2 were from 10^{-2} to 10^{-1} in magnitude at 40–60 °C, but the decomposition constants k_{-2} of 3-(β-hydroxy-ethylsulfonyl)-nitrobenzene were two orders in magnitude smaller than that of corresponding vinyl-sulfone hydration.
3. The average apparent activation energies were calculated by Arrhenius equations: $E_1 = 111.42$ kJ/mol; $E_{-1} = 57.72$ kJ/mol; $E_2 = 97.23$ kJ/mol; and $E_{-2} = 79.16$ kJ/mol.
4. The optimized condition of alkaline hydrolysis of 2,2′-(3″-nitrobenzenesulfonyl)-ethyl ether (E) was carried out in a 1–3% sodium carbonate solution at boiling temperature for 1 h with a $\geq 96\%$ yield of 3-(β-hydroxy-ethylsulfonyl)-nitrobenzene (H) and $\geq 97\%$ in product purity.

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