J. Org. Chem. 1982, 47, 2879–2882

Kinetics of Oxidation of Anthracene by Use of Copper(II) Chloro Complexes in a Mixture of Acetic Acid and Water

Jinya Koshitani,* Toshio Kado, Yoshio Ueno, and Takatoshi Yoshida

Department of Industrial Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan

Received September 18, 1981

The kinetics of initial rates of consumption of substrate in the oxidation of anthracene (AN) at 90 °C by use of copper(II) chloro complexes in a mixture of acetic acid and water were studied, and the relationship between initial rates of consumption of substrate and initial rates of oxygen absorption was investigated. The following results were obtained. The rates of disappearance of anthracene and oxygen are approximately equal: $-d[AN]/dt \propto [AN]^1[Cu_2(OAc)_4]_{initial}^{1/2-0}[NaCl]_{initial}^{1-0}$.

It is generally known that polynuclear aromatic hydrocarbons are not oxidized readily in autoxidations.[1] This is due in large part to the fact that the rates of the reactions between aryl radicals and oxygen molecules are slow and that radical terminations participate in the oxidations. We reasoned that some compound which could serve both as an oxidant and a radical scavenger might make the oxidation of a polynuclear aromatic hydrocarbon progress more readily. The liquid-phase oxidation[2] of the polynuclear aromatic hydrocarbon by use of copper(II) acetate, which possesses the above two properties,[3-12] and alkaline halide was tried and progressed readily. In this report, the initial rates of consumption of substrate and the initial rates of oxygen absorption were measured in the oxidation of anthracene (AN) at 90 °C by use of copper(II) acetate and sodium chloride in a mixture of acetic acid and water. In particular, the relationship between the initial rates of consumption of substrate and the initial rates of oxygen absorption were investigated.

Results and Discussion

Reaction and Products. Anthracene was reacted with oxygen, copper(II) acetate, and sodium chloride. The major reaction products were anthraquinone (**9**) and anthrone (**10**), while a trace of 9-acetoxyanthracene was detected. No 10,10′-bianthrone or carbon dioxide was detected. Typical patterns of consumption of substrate, production of **9** and **10**, and oxygen absorption in the oxidation, under the conditions of a 0.05 M initial concentration of substrate, a 0.005 M initially added concentration of copper(II) acetate as the dimer, and a 0.01 M initially added concentration of sodium chloride, are shown in Figure 1. The amount of **9** produced increased with the passage of time. On the other hand, at the initial stage of oxidation, the amount of **10** produced was the same as the amount of **9**. The amount of **10** produced increased with the passage of time, but at a slower rate than the production of **9**. Further, the amount of **10** produced approached a maximum at about 300 min and afterward gradually decreased. The patterns of consumption of AN and oxygen absorption were steady. It is generally known that polynuclear aromatic hydrocarbons are not readily oxidized in liquid-phase oxidation, and the low rate of the elementary reaction of radicals with oxygen molecule and terminations which are related to the radicals are the causes[1] of this phenomenon. However, it is stressed that this liquid-phase oxidation progresses in spite of the hindrance. To determine whether peroxide is produced or not, we investigated the reaction mixture by iodometry.[13,14] It seemed that the amount of peroxide in the reaction solution was very small. A variation of the visible spectrum after the beginning of the reaction was small. Thus, it is presumed that there were not prominent variations in kinds and amounts of species, copper(II) salts and copper(II) complexes, during the measurement of the initial rate of oxygen absorption.

Table I. Effect of the Concentration of Substrate on the Rate of Consumption of Substrate

reaction time, min	$\ln [AN]^a/[AN]_t^b$	$10^5 k_{obsd}{}^c$
60	0.15	4.1
180	0.37	3.4
292	0.56	3.2
400	0.73	3.0

[a] [AN] = the initial concentration of anthracene.
[b] $[AN]_t$ = the concentration of anthracene at the reaction time *t*. [c] $k_{obsd} = 1/t \ln [AN]/[AN]_t$.

Kinetic Studies. The effect of the concentration of substrate on the rate of consumption of substrate was investigated at initially added concentrations of 0.05 M substrate, 0.005 M copper(II) acetate dimer, and 0.01 M sodium chloride. The initial rate of consumption of substrate showed nearly first-order dependence with respect to the initial concentration of substrate (Table I). The effect of the concentration of substrate on the rate of oxygen absorption was investigated when the initial concentration of substrate was maintained at a succession of varying values within the range 0.005–0.05 M at initial concentrations of 0.005 M copper(II) acetate dimer and 0.01 M sodium chloride. The initial rate of oxygen absorption showed about first-order dependence with respect

---

(1) Y. Kamiya, "Yūki Sanka Hannō", Gihōdō, Tokyo, 1973, pp 371.
(2) J. Koshitani, M. Hiramatsu, Y. Ueno, and T. Yoshida, *Bull. Chem. Soc. Jpn.*, **51**, 3667 (1978).
(3) J. K. Kochi and R. V. Subramanian, *Inorg. Chem.*, 4, 1527 (1965).
(4) M. Weiss and M. Appel, *J. Am. Chem. Soc.*, **70**, 3666 (1948).
(5) N. R. Campbell, J. H. Dunsmuir, and M. E. H. Fitzgerald, *J. Chem. Soc.*, 2743 (1950).
(6) I. A. Pearl, *J. Am. Chem. Soc.*, 74, 4260 (1952).
(7) A. T. Blomquist, L. H. Liu, and J. C. Bohrer, *J. Am. Chem. Soc.*, 74, 3643 (1952).
(8) E. E. van Tamelen, T. A. Spencer, D. S. Allen, and D. L. Orvis, *J. Am. Chem. Soc.*, 81, 6341 (1959).
(9) M. L. Lewbart and V. R. Mattox, *J. Org. Chem.*, **28**, 2001 (1963).
(10) J. K. Kochi and R. V. Subramanian, *J. Am. Chem. Soc.*, **87**, 4855 (1965).
(11) C. L. Jenkins and J. K. Kochi, *J. Am. Chem. Soc.*, **94**, 843 (1972).
(12) C. Giordano, A. Belli, A. Citterio, and F. Minisci, *J. Org. Chem.*, **44**, 2314 (1979).
(13) C. D. Wagner, R. H. Smith, and E. D. Peters, *Ind. Eng. Chem., Anal. Ed.*, **19**, 976 (1947).
(14) R. D. Mair and A. J. Graupner, *Anal. Chem.*, **36**, 194 (1964).

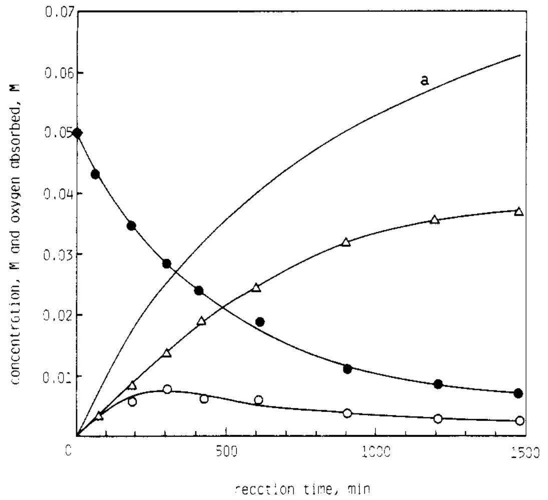


Figure 1. Time course of the oxidation: AN (●), **9** (△), **10** (○), oxygen absorbed (a).

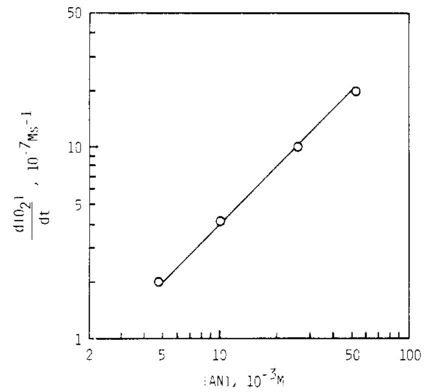


Figure 2. Effect of the concentration of substrate on the rate of oxygen absorption.

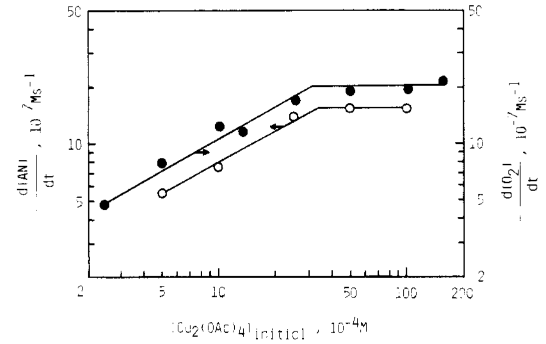


Figure 3. Effects of the concentration of copper(II) acetate on the rates of consumption of substrate and oxygen absorption.

to the initial concentration of substrate (Figure 2).

The effects of the concentration of copper(II) acetate on the rates of consumption of substrate and oxygen absorption were investigated at initially added concentrations of 0.05 M substrate and 0.01 M sodium chloride. The results are shown in Figure 3. In the 0.0005–0.0025 M initially added concentration range of copper(II) acetate dimer, the initial rate of consumption of substrate showed about half-order dependence with respect to the initially added concentration of copper(II) acetate dimer. On the other hand, at a higher initially added concentration of the copper(II) acetate dimer (0.0025–0.01 M), the initial rate of consumption of substrate approached zero-order dependence with respect to the initially added concentration of copper(II) acetate dimer. The initial rate of oxygen absorption showed about half-order dependence with respect to the initially added concentration of copper(II) acetate dimer (0.000 25–0.0025 M) and approached zero-order dependence with respect to the initially added concentration of copper(II) acetate dimer (at higher concentration).

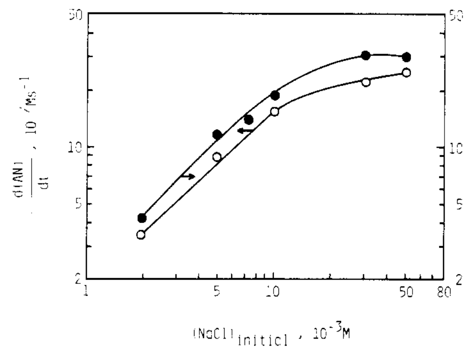


Figure 4. Effects of the concentration of sodium chloride on the rates of consumption of substrate and oxygen absorption.

The effects of the concentration of sodium chloride on the rates of consumption of substrate and oxygen absorption were investigated at initially added concentrations of 0.05 M substrate and 0.005 M copper(II) acetate dimer. The results are shown in Figure 4. The initial rate of consumption of substrate showed about first-order dependence with respect to the initially added concentration of sodium chloride (0.002–0.01 M) and approached zero-order dependence with respect to the initially added concentration of sodium chloride (at higher concentration). The initial rate of oxygen absorption showed about first-order dependence with respect to the initially added concentration of sodium chloride (0.002–0.01 M) and approached zero-order dependence with respect to the initially added concentration of sodium chloride (at higher concentration).

From the kinetic studies, the following rate laws can be written:

$$-d[AN]/dt \propto [AN]^1[Cu_2(OAc)_4]^{1/2-0}_{initial}[NaCl]^{1-0}_{initial} \quad (1)$$

$$-d[O_2]/dt \propto [AN]^1[Cu_2(OAc)_4]^{1/2-0}_{initial}[NaCl]^{1-0}_{initial} \quad (2)$$

Order dependences of initial rates of consumption of substrate and oxygen absorption were the same, regardless of the initial concentration of substrate, the initially added concentration of copper(II) acetate dimer, and the initially added concentration of sodium chloride, respectively.

Kinetic Approximation. It is generally accepted that mechanisms of autoxidation of anthracene are complex and that the mechanisms are not strictly decided. Here, on the basis of kinetics, an approximation to the experimental fact was tried: M(II) and M(I) respectively indicate copper(II) ion and copper(I) ion as active species, and eq 3

$$[M(II)] \propto [Cu_2(OAc)_4]^{1/2-0}_{initial}[NaCl]^{1-0}_{initial} \quad (3)$$

is assumed. A one-electron-transfer reaction between AN and M(II) may be important as the first step in this oxidation (eq 4, Scheme I). The radical cation **1** may lose a proton to yield 9-anthryl radical (**2**, eq 5). Similar reactions have been reported by Andrulis et al.,[15] Aratani and Dewar,[16] and Heiba et al.[17] The **2** yielded may react with oxygen to form 9-anthrylperoxy radical (**3**, eq 6). **3** may abstract a hydrogen atom from AN to give **4** and **2**

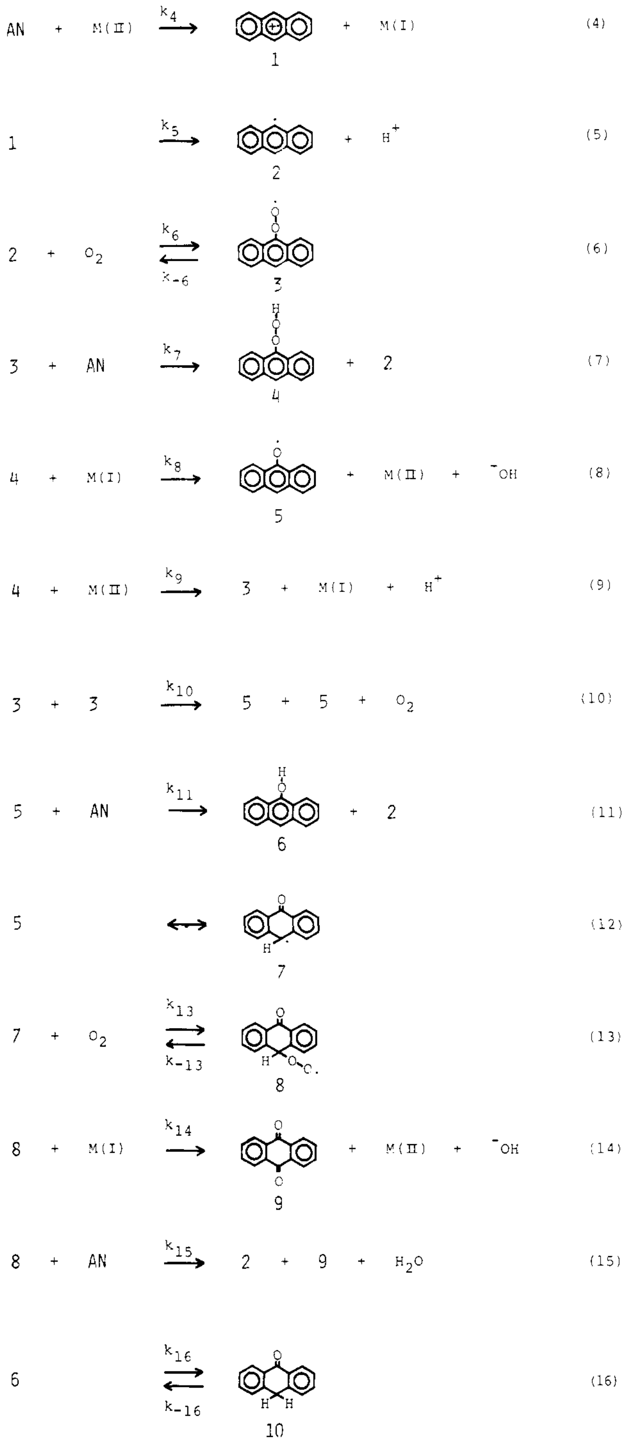
---

[15] P. J. Andrulis, Jr., M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Am. Chem. Soc.*, **88**, 5473 (1966).

[16] T. Aratani and M. J. S. Dewar, *J. Am. Chem. Soc.*, **88**, 5479 (1966).

[17] E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **91**, 6830 (1969).

Scheme I



(eq 7). 4 may be decomposed by M(I) and M(II) (eq 8 and 9). It is known that reactions of metal ions with hydroperoxide are important initiation steps.[18,19] A bimolecular reaction of 3 with another molecule of 3 seems to yield two 9-anthryloxy radicals (5) and oxygen (eq 10). 5 may abstract a hydrogen atom from AN to produce 9-anthranol (6) and 2 (eq 11). On the other hand, 5 may resonate to the 10-anthronyl radical (7) as reported by Ogata et al.[20] and Yoshida et al.[21] (eq 12). 7 may react with oxygen to give (10-anthronyl)peroxy radical (8, eq 13).[20,21] On the basis of other works,[22-24] we thought that 8 might react with M(I) and AN (eq 14 and 15). An equilibrium[25,26] between 6 and 10 is reported (eq 16). Therefore, in the early stage of the oxidation, eq 17–21 are derived from eq 4–16 of Scheme I (Appendix). The results of these calculations fit in with the experimental facts.

$$-\mathrm{d}[\mathrm{AN}]/\mathrm{d}t \simeq 2k_4[\mathrm{AN}][\mathrm{M(II)}] \tag{17}$$

$$\mathrm{d}[\mathbf{9}]/\mathrm{d}t = k_4[\mathrm{AN}][\mathrm{M(II)}] \tag{18}$$

$$\mathrm{d}[\mathbf{10}]/\mathrm{dt} \simeq k_4[\mathrm{AN}][\mathrm{M(II)}] \tag{19}$$

$$(-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t)/(\mathrm{d}[\mathbf{9}]/\mathrm{d}t) \simeq 2 \tag{20}$$

$$(-\mathrm{d}[\mathrm{AN}]/\mathrm{d}t)/(-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t) \simeq 1 \tag{21}$$

Experimental Section

Materials. Oxygen (commercial gas), copper(II) acetate (reagent grade), sodium chloride (reagent grade), and acetic acid (reagent grade) were respectively purified by conventional methods. By the method of Takeuchi and Furusawa,[27] AN (reagent grade) was dissolved in xylenes, and the solution was added to methanol. Then the solution was filtered, and the AN was dried under vacuum. **9** was purified by using the method of Tsuchida et al.[28] **10** was synthesized from **9** according to the method described by Meyer.[29] 9-Acetoxyanthracene was synthesized by using the method by Meek et al.[30]

Oxidation Procedure. Oxidation was performed in a closed system by use of an oxidation apparatus equipped with a gas buret in a mixture of acetic acid and water (mole fraction of water = 26%) at 90 °C. The reaction was performed under a 3.8×10^2-mmHg partial pressure of oxygen, by which the rate of oxidation was not affected. Oxygen absorption was followed by a manually controlled gas buret filled with mercury.

Measurements. A visible spectrophotometer, mass spectrometer, gas chromatograph–mass spectrometer, gas chromatograph, and NMR spectrometer were utilized for measurement of visible spectra of the reaction solution and for identification and quantitative analyses of the reaction products in comparison with authentic samples. Analysis of peroxide was performed by the method reported by Wager et al.[13] and by the method of Mair and Graupner.[14]

Appendix

Derivation of Eq 17-21. Steady-state treatment is applied. Therefore,

$$-\frac{\mathrm{d}[\mathrm{AN}]}{\mathrm{d}t} = (k_4[\mathrm{AN}][\mathrm{M(II)}] + k_9[\mathbf{4}][\mathrm{M(II)}]) \times \left(1 + \frac{k_{11}[\mathrm{AN}]}{k_{13}[\mathrm{O_2}]}\left(1 + \frac{k_{-13} + k_{15}[\mathrm{AN}]}{k_{14}[\mathrm{M(I)}]}\right) + \frac{k_{15}[\mathrm{AN}]}{k_{14}[\mathrm{M(I)}]}\right)$$

$$\frac{\mathrm{d}[\mathbf{9}]}{\mathrm{d}t} = (k_4[\mathrm{AN}][\mathrm{M(II)}] + k_9[\mathbf{4}][\mathrm{M(II)}])\left(1 + \frac{k_{15}[\mathrm{AN}]}{k_{14}[\mathrm{M(I)}]}\right)$$

---

[18] F. Haber and J. Weiss, *Proc. R. Soc. London, Ser. A*, **147**, 332 (1934).

[19] J. Weiss, *Trans. Farady Soc.*, **31**, 1547 (1935).

[20] Y. Ogata, Y. Kosugi, and K. Nate, *Tetrahedron*, **27**, 2705 (1971).

[21] T. Yoshida, Y. Ueno, and S. Wakabayashi, *Kogyo Kagaku Zasshi*, **72**, 338 (1969).

[22] Y. Ogata, K. Nate, and M. Yamashita, *Bull. Chem. Soc. Jpn.*, **47**, 174 (1974).

[23] E. C. Horswill and K. U. Ingold, *Can. J. Chem.*, **44**, 263 (1966).

[24] E. C. Horswill and K. U. Ingold, *Can. J. Chem.*, **44**, 269 (1966).

[25] K. H. Meyer, *Justus Liebigs Ann. Chem.*, **379**, 37 (1911).

[26] Y. Bansho and K. Nukada, *Kogyo Kagaku Zasshi*, **63**, 620 (1960).

[27] T. Takeuchi and M. Furusawa, *Kogyo Kagaku Zasshi*, **68**, 474 (1965).

[28] E. Tsuchida, Y. Miyake, T. Kawagoe, and I. Shinohara, *Kogyo Kagaku Zasshi*, **71**, 1572 (1968).

[29] K. H. Meyer, "Organic Syntheses", Collect. Vol. I, Wiley, New York, 1963, p 60.

[30] J. S. Meek, P. A. Monroe, and C. J. Bouboulis, *J. Org. Chem.*, **28**, 2572 (1963).

$$\frac{\mathrm{d}[\mathbf{10}]}{\mathrm{d}t} = \frac{k_{11}[\mathrm{AN}]}{k_{13}[\mathrm{O_2}]}\left(1 + \frac{k_{-13} + k_{15}[\mathrm{AN}]}{k_{14}[\mathrm{M(I)}]}\right)(k_4[\mathrm{AN}] \times [\mathrm{M(II)}] + k_9[\mathbf{4}][\mathrm{M(II)}])$$

$$-\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} = (k_4[\mathrm{AN}][\mathrm{M(II)}] + k_9[\mathbf{4}][\mathrm{M(II)}])\left(\frac{3}{2} + \frac{3}{2}\left(\frac{k_{15}[\mathrm{AN}]}{k_{14}[\mathrm{M(I)}]}\right) + \frac{k_{11}[\mathrm{AN}]}{2k_{13}[\mathrm{O_2}]}\left(1 + \frac{k_{-13} + k_{15}[\mathrm{AN}]}{k_{14}[\mathrm{M(I)}]}\right)\right)$$

Since [**4**] may be very small

$$k_4[\mathrm{AN}]/[\mathbf{4}] \gg k_9$$

The relation between the rate of production of **10** and the rate of production of **9** is represented as

$$\frac{\mathrm{d}[\mathbf{10}]}{\mathrm{d}t} = F\,\frac{\mathrm{d}[\mathbf{9}]}{\mathrm{d}t}$$

where F is a function. Therefore

$$(-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t)/(\mathrm{d}[\mathbf{9}]/\mathrm{d}t) = (3 + F)/2$$

$$\frac{-\mathrm{d}[\mathrm{AN}]/\mathrm{d}t}{-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t} = \frac{1 + \mathrm{F}}{3/2 + F/2}$$

If $k_{14}[\mathrm{M(I)}] \gg k_{15}[\mathrm{AN}]$

$$-\mathrm{d}[\mathrm{AN}]/\mathrm{d}t = (1 + F)k_4[\mathrm{AN}][\mathrm{M(II)}]$$

Here, F may be decided on the basis of experimental fact. For example, in the experimental result (Figure 1), F is nearly constant in the initial stage of the oxidation at a value of about 1. Therefore, in the early stage of the oxidation

$$-\mathrm{d}[\mathrm{AN}]/\mathrm{d}t \simeq 2k_4[\mathrm{AN}][\mathrm{M(II)}] \quad (17)$$

$$\mathrm{d}[\mathbf{9}]/\mathrm{d}t = k_4[\mathrm{AN}][\mathrm{M(II)}] \quad (18)$$

$$\mathrm{d}[\mathbf{10}]/\mathrm{d}t \simeq k_4[\mathrm{AN}][\mathrm{M(II)}] \quad (19)$$

$$(-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t)/(\mathrm{d}[\mathbf{9}]/\mathrm{d}t) \simeq 2 \quad (20)$$

$$(-\mathrm{d}[\mathrm{AN}]/\mathrm{d}t)/(-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t) \simeq 1 \quad (21)$$

Registry No. Anthracene, 120-12-7; copper(II) acetate, 142-71-2; sodium chloride, 7647-14-5.

Preparation of Chiral 1-Deuteriobenzenemethanethiols by Using α′,β Elimination of Carbanions Derived from Benzylic Thioethers

Jean-François Biellmann* and Hugues d'Orchymont

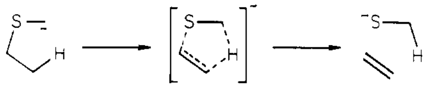
Laboratoire de Chimie Organique Biologique, Associé au CNRS, Institut de Chimie, Université Louis Pasteur, 67008 Strasbourg, Cedex, France

Received January 22, 1982

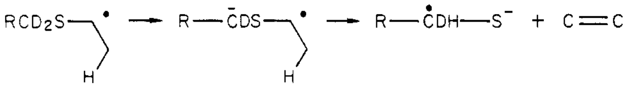
The α′,β elimination of the carbanion derived from [α-$^2H_2$]benzyl isolongifolyl thioether and [α-$^2H_2$]benzyl camphyl thioether gives the chiral [α-^{2}H]benzyl mercaptan, the S isomer with 38 ± 6% ee and the R isomer with 49 ± 7% ee. The chirality of the [α-^{2}H]benzyl mercaptan was determined by optical rotation of [α-^{2}H]benzyl methyl thioether and thiosulfone. The enantiomeric excess was evaluated from ^{1}H NMR measurement of ethyl (benzylthio)phenylacetate prepared from (−)-mandelic acid. The enantiomeric excess at carbon C-2 of ethyl (benzylthio)phenylacetate was determined with a chiral europium chelate and was about 60%. These results are discussed with reference to the transition state of the α,β elimination and to related processes.

We report here a direct method for the preparation of chiral [α-^{2}H]benzenemethanethiol. The tedious synthesis of thioaldehydes renders unattractive attempts to achieve their asymmetric reduction by the methods used for the conversion of aldehydes to 1-deuterio primary alcohols.[1–3] The absence of a reaction analogous to the Baeyer–Villiger reaction for a stereospecific sulfur insertion into a C–C bond is also a strong limitation. The high nucleophilic character of thiolates has been widely used in the substitution reaction of activated derivatives of a chiral 1-deuterio primary alcohol to the mercaptan or thioether.[4,5] However, the possibility of chirality on a sulfur atom provides new alternatives. For instance, a neighboring chiral group such as sulfoxide or sulfimine can induce a stereospecific introduction of the label, as was shown with benzyl methyl sulfoxide.[6]

The α′,β elimination of carbanions derived from the thioether proceeds in high yields, and its stereochemical course is in agreement with a syn elimination mechanism.



The large primary isotope effect observed with benzyl cyclooctyl thioether (7.0–9.0) indicates that the α-carbon is close to the proton being transfered from the β-carbon.[7] This prompted the idea that, by using a chiral proton-donating group, the chiral thiol may be prepared in a direct fashion. However, the large primary isotope effect is likely to render impractical a reaction scheme where deuterium is transferred, owing to the increase in the number of side



---

[1] Arigoni, D.; Eliel, E. L. *Top. Stereochem.*, **1969**, *4*, 127.

[2] Morrison, J. D.; Mosher, H. S. "Asymetric Organic Reactions"; American Chemical Society: Washington, DC, 1976.

[3] Midland, M. M.; Greer, S.; Tromantano, A.; Zderic S. A. *J. Am. Chem. Soc.* **1979**, *101*, 2352.

[4] Miller, E. G.; Rayner, D. R.; Thomas, H. T.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4861.

[5] Kice, J. L.; Engebrecht, R. H.; Pawlowski, N. E. *J. Am. Chem. Soc.* **1965**, *87*, 4131.

[6] Durst, T.; Viau, R.; McClory, M. R. *J. Am. Chem. Soc.* **1971**, *93*, 3077.

[7] Biellmann, J. F.; d'Orchymont, H.; Schmitt, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 3283.