added Me_4Si internal standard showed a singlet at δ 8.6 as well as the upfield adamantyl peaks. Subsequent solvent removal (at 132 °C) yielded 203 mg of an oil. An infrared spectrum showed a peak at 2900 cm^{-1} as the only strong band; medium strength bands appeared at 1601, 1580, 1470, and 1440 cm^{-1}. ^{1}H NMR spectroscopy showed peaks at δ 7.60 (s), a multiplet centered at δ 7.20, and broad adamantyl peaks centered at δ 1.80 with integration ratio 1:6:15. These results suggest that **7** initially yields a sulfenimine.[34] Preparative TLC gave three bands. Extraction with ether and characterization indicated extensive decomposition of original compound to two products: diphenyl disulfide (80.5 mg) and adamantylcarboxaldehyde (110 mg, 82%), which proved identical with an authentic sample.

Thermolysis of α-Azido-1-adamantylmethyl Phenyl Sulfoxide (8). A solution of 150 mg of **8** (mixture of diastereomers) was treated in a similar manner (120 °C for 1 h) to give the sulfide analogue above. Gas chromatographic analysis using *n*-hexadecane as internal standard showed the presence of diphenyl disulfide (20 mg), adamantylcarbonitrile (21.8 mg, 28.5%), adamantylcarboxaldehyde (3.2 mg, 4.1%), and phenylthiobenzenesulfonate (45 mg).

Kinetic Experiments. The thermal decomposition of α-azidobenzyl phenyl sulfide was followed by the gas evolution method in four different solvents.[2] Good first-order rate constants were obtained and are summarized in Table I.

The pyrolysis of α-azidobenzyl phenyl sulfoxide in chlorobenzene was monitored by ^{1}H NMR spectroscopy. The decrease in integration for δ 5.77 benzylic proton peak as a ratio to the silicon oil peak (added as internal standard) was observed. The resultant first-order rate constants showed good correlation $r > 0.98$. Table II summarizes these data.

The same procedure as for the latter case was followed for determination of first-order constants of α-azido-1-adamantylmethyl phenyl sulfide (**7**) and sulfoxide (**8**). In this case, the diminishment of methyl proton peaks were followed. Rate constant for **7** at 130 °C was $3.25 \pm 0.21 \times 10^{-4}$ s^{-1}, while that of **8** at 110 °C was $2.04 \pm 0.13 \times 10^{-3}$ s^{-1}; both determinations were carried out in chlorobenzene.

CIDNP Experiments. ^{1}H NMR spectra were obtained on a Varian FT-80A instrument operating at 80 MHz in the Fourier transform mode. Ten milligrams of α-azidobenzyl phenyl sulfoxide (**3**) was dissolved in $\simeq$0.4 mL of carbon tetrachloride and 0.2 mL of dioxane-d_8 (^{2}H lock) in a 5-mm tube. Approximately 60–90 s was needed for thermal equilibration after which single transient FID pulses (40 μs pulse, 80° flip angle, 1 kHz spectral width, 4.096 data points) were obtained and stored on a "floppy" disc. The spectra were then transformed after 30 min of collection. Similar procedures were repeated for **3** at 76 °C but with dimethyl-d_6 sulfoxide (^{2}H lock) and for α-azidobenzyl phenyl sulfide (**1**) at 118 °C in tetrachloroethylene and dioxane-d_8. Spectra for sulfoxide **3** are shown in Figure 1.

Acknowledgment. P. E. Nicholas thanks the Gillette Corp. for a fellowship. We also acknowledge Dr. E. P. Mazzola, FDA, Washington, DC, for assistance in the CIDNP experiments.

---

[33] Almog, J.; Barton, D. H. R.; Magnus, P. D. *J. Chem. Soc., Perkin Trans. 1* **1974**, 853.

[34] Unsymmetrical sulfenimines are known to exist as geometric isomers which are interconvertible (see Carr, E. L.; Smith, Jr., G. E. P.; Alliger, G. *J. Org. Chem.* **1949**, *14*, 921). Apparently the less stable isomer in this case has its imidoyl ^{1}H NMR peak at δ 8.6, while the more stable isomer exhibits the peak at δ 7.6.

Oxygenation with Molecular Oxygen. Thermal and Photochemical Epoxidation of Propylene in the Presence of Sulfur Dioxide in Acetonitrile at Ambient Temperature

Tadahiro Sasaki

Contribution from the Chemicals Research Laboratory, Showa Denko Co., 5-1 Oogi-Machi, Kawasaki-Ku, Kawasaki 210, Japan.

Received November 10, 1980

Abstract: Irradiation of a mixture of propylene and sulfur dioxide in acetonitrile at ice-cold temperature causes absorption of molecular oxygen and gives propylene oxide as the sole volatile product. Also, in the absence of light, the addition of nitrite or nitrate salts to a mixture of sulfur dioxide and propylene in acetonitrile under oxygen at room temperature leads to the smooth formation of propylene oxide as the only volatile product. Both reactions show quite similar solvent dependence and are retarded by the additives with ionizaiton potentials lower than ca. 9.5 eV. The main byproduct is poly(propylenesulfonate). The mechanisms of the epoxidation reactions are discussed.

The reactivity of molecular oxygen has been the subject of great interest from both practical and theoretical points of view.[1] The ability to use oxygen in a procedure which selectively oxidizes organic compounds under mild conditions would surely be desirable. Much research and debate are now concentrating on oxygenation via non-singlet-oxygen mechanisms, especially ones which involve electron-transfer processes to produce epoxides.[2] We here report a new reaction system in which molecular oxygen oxidizes olefins to epoxides both thermally and photochemically in the presence of sulfur dioxide under ambient conditions. Since propylene has the combination of solubility, reaction rate, and ease of product detection under our present conditions, it is most suited for the initial study on these interesting but rather complex reactions reported here.

Photochemical Reactions

The irradiation of a mixture of propylene and sulfur dioxide in oxygen-saturated acetonitrile with a 400 W medium-pressure mercury-arc lamp through Pyrex at an ice-cold temperature produces propylene oxide essentially as the only volatile product. The formation of propylene oxide was confirmed by GC/mass analysis of the reaction mixture and the infrared and NMR spectra of the isolated product. Two other products are obtained. One is a viscous and colorless liquid which is obtained when the solvent is removed from the reaction mixture (see below for the structure determination of the nonvolatile sulfur-containing product). The other is a white solid which settles out on the reaction vessel wall during irradiation sporadically from run to run. The solid was easily identified as poly(propylene sulfone)[3] by the infrared

---

[1] (a) Hayaishi, O., Ed. "Molecular Mechanisms of Oxygen Activation"; Academic Press: New York, 1974. (b) Wasserman, H. H.; Murray, R. W., Eds. "Singlet Oxygen"; Academic Press: New York, 1979. (c) Emanuel', N. M., Ed. "The Oxidation of Hydrocarbons in the Liquid Phase"; Pergamon Press: Oxford, 1965.

[2] (a) Bartlett, P. D. In "Organic Free Radicals", Pryor, W. A., Ed.; American Chemical Society: Washington, D.C., 1978; p 15. (b) Ando, W.; Kabe, Y.; Kobayashi, S.; Takyu, C.; Yamagishi, A.; Inaba, H. *J. Am. Chem. Soc.* **1980**, *102*, 4526.

[3] Hunt, M.; Marvel, C. S. *J. Am. Chem. Soc.* **1935**, *57*, 1691.

0002-7863/81/1503-3882$01.25/0

spectrum, decomposition point, and elemental analysis. The amount of poly(propylene sulfone) is negligibly small immediately after the reaction. The mole ratio of the propylene unit contained in the viscous liquid to that of propylene oxide is usually 2–4.

The striking feature of the reaction is the effect of the reaction medium. Propylene oxide cannot be obtained in solvents such as benzene, toluene, xylene, carbon tetrachloride, chloroform, dichloromethane, carbon disulfide, cyclohexane, and dioxane. Formation of propylene oxide can be observed in acetonitrile, propionitrile, acetone, ethyl acetate, acetic anhydride (propylene glycol diacetate is the main product), acetic acid, methanol, and nitromethane. Addition of phenols (2,6-di-*tert*-butyl-*p*-cresol and hydroquinone), amines (e.g., pyridine and 1,4-diazabicyclo[2.2.2]octane), or aromatic compounds (naphthalene, diphenyl ether, etc.) retards the epoxidation reaction. A closer examination of the effect of the solvents and additives shows that their ionization potentials[4] and dielectric constants are important in controlling the reaction. When solvents have ionization potentials higher than ca. 9.5 eV and dielectric constants larger than ca. 10 (20 °C), the epoxidation reaction proceeds. Acetonitrile is the most favorable solvent. Epoxide formation cannot be observed in solvents with ionization potentials lower than ca. 9.5 eV and/or dielectric constants smaller than ca. 10. Additives with ionization potentials lower than ca. 9.5 eV retard the reaction. The absence of any one component in the O_2–SO_2–propylene–solvent–light system does not give the epoxide. Irradiation at $\lambda > 500$ nm or with light containing shorter wavelength (<280 nm) does not give propylene oxide. Propylene oxide is not very stable under the reaction conditions and is gradually converted to some polymeric products. Thus, it is rather surprising that propylene oxide can be observed in a sufficient amount after the photochemical reaction.

Thermal Reactions

Since epoxides are not stable under the photochemical reaction conditions, a thermal counterpart was sought in order to investigate the nature of the reaction more quantitatively. We could find that the same type (or at least quite similar type) of epoxidation reaction can proceed effectively without light at room temperature with the addition of nitrite or nitrate salts to a mixture of sulfur dioxide and propylene in oxygen-saturated acetonitrile. For example, oxygen absorption could be immediately observed at room temperature after the addition of potassium nitrite (10 mmol) to a mixture of sulfur dioxide (99 mmol) and propylene (20 mmol) in acetonitrile (100 mL). The amount of propylene oxide thus formed after 8 h is 6 mmol with 7.5 mmol of oxygen uptake and 11.5 mmol of sulfur dioxide loss. Figure 1 shows a case in which oxygen and propylene were bubbled through a mixture of potassium nitrite and sulfur dioxide in acetonitrile. Propylene oxide is essentially the only volatile product. The added nitrite salt gradually changes into potassium sulfate during the reaction. The other product is a colorless viscous liquid which is obtained from the reaction mixture after the removal of the solvent (see below for the structure determination). Poly(propylene sulfone) formation is not observed in the reaction. The amount of the epoxide formed is usually two to three times that of the consumed nitrite salt in moles. The ratio of the propylene unit in the viscous liquid to that of propylene oxide is now reduced to approximately 1–2 in moles.

Interestingly, the solvent dependence and the effect of additives are quite similar to that of the photochemical epoxidation of propylene in the presence of sulfur dioxide. Alcohols and acidic solvents like acetic acid are not favorable to the reaction in the presence of nitrite or nitrate salts probably because of the reactivity of the solvents with the salts. The presence of additives or solvents with ionization potentials lower than ca. 9.5 eV retards the oxidation reaction. For example, addition of pyridine (IP 9.25 eV) retards the reaction while addition of 4-cyanopyridine (IP >10)[5] does not. In solvents with ionization potentials higher than ca. 9.5 eV but with small dielectric constants ($\epsilon < 10$) the thermal reaction either does not occur or proceeds very slowly.

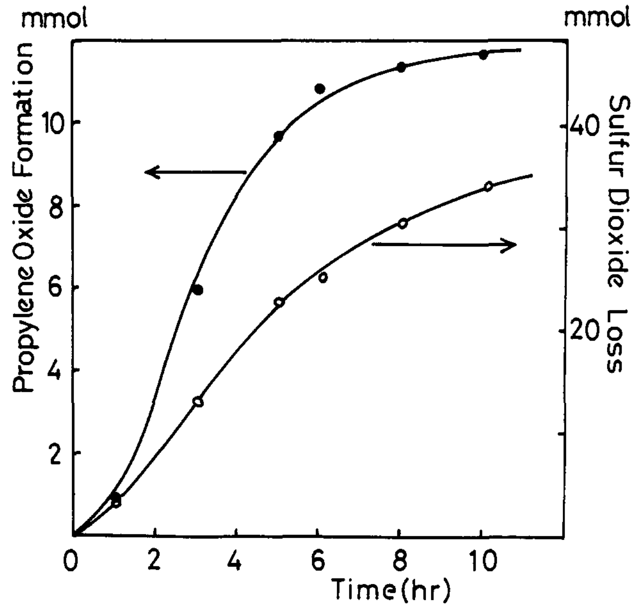


Figure 1. Formation of propylene oxide and loss of sulfur dioxide in the potassium nitrite added reaction. Solvent, acetonitrile; potassium nitrite, 5.47 mmol; sulfur dioxide, 56.2 mmol; oxygen, 10.7 mL/min; propylene, 9.5 mL/min. Temperature, 26 °C.

Nitrite salts are usually more effective than nitrates. The only unique case among the salts tested in our hands is with palladium salts ($K_2[Pd(NO_2)_4]$ and $Pd(NO_3)_2$). Acetone is the only volatile product in the presence of the palladium salts.[6] Both propylene oxide and acetone are close to being stable under the reaction conditions.

Structure of the Nonvolatile Products

The nonvolatile product (viscous liquid, colorless to straw yellow) formed in the photochemical and that formed in the thermal reactions are similar in structure. The infrared spectra of the products from both reactions show strong absorptions at 1360 and 1170 cm^{-1} and are almost identical except for the presence of characteristic absorptions at 1565 and 1640 cm^{-1} in the spectrum of the thermal reaction product. The major component of the viscous liquid formed in the photochemical reaction has a molecular weight distribution centered at around 3000 (gel permeation analysis, see Experimental Section) and an approximate formula of $C_3H_6O_3S$. The S=O region absorptions (1360 and 1170 cm^{-1}) of the infrared spectrum resemble those of 1,3-propane sultone (1,2-oxathiolane 2,2-dioxide) and are distinctly different from those of poly(ethylenesulfite).[7] Thus we tentatively assign the structure of the polymer as poly(propylenesulfonate). The secondary product obtained in a product stability study by the reaction of propylene oxide with sulfur dioxide under the photochemical reaction conditions has a somewhat different structure from that of the poly(propylenesulfonate).

The thermolysis of the poly(propylenesulfonate) gives propylene, acetone, sulfur dioxide, and some charred solids. About 30% of the propylene component can be recovered.

The major fraction of the nonvolatile product formed in the thermal reaction has structural features similar to those of the

---

[4] The use of oxidation and reduction potentials in acetonitrile may be preferable. For correlations of oxidation and reduction potentials with ionization potentials, see: Parker, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 98. The ionization potentials used here were taken from "Handbook of Chemistry and Physics", Weast, R. C., Ed.; The Chemical Rubber Co.: Cleveland, Ohio, 1969; College Edition; "Kagaku Binran", Kisohen, Chemical Society of Japan, Maruzen Co.: Tokyo, 1975.

[5] The ionization potential is estimated to be larger than 10 eV since 4-chloropyridine has the value of 10.3 eV.

[6] Acetone is not the secondary product by the isomerization of propylene oxide. Addition of propylene oxide in the starting reaction mixture retarded the formation of acetone. The case can be considered to be a nonaqueous Wacker process.

[7] Soga, K.; Hattori, I; Kinoshita, J.; Ikeda, S. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 745.

Table I. Stereochemistry in the Epoxidation of *cis*- and *trans*-2-Butenes

olefins[a] (mmol)	reaction conditions[b]	oxygen absorption, mmol	trans/cis	
			epoxide[c]	olefin[d]
cis-2-butene (75)	SO_2 54 mmol, irradiated for 3.5 h	2.7	90/10	37/63
trans-2-butene (41)	SO_2 65 mmol, irradiated for 3 h	1.9	95/5	81/18
cis-2-butene (88)	SO_2 58 mmol, KNO_2 10 mmol, 5 h at room temp	4.0	78/22	8/92
trans-2-butene (58)	SO_2 49 mmol, KNO_2 10 mmol, 5 h at room temp	5.4	97/3	98.3/1.7

[a] *cis*-2-Butene contains 2% of the trans isomer. *trans*-2-Butene has more than 99% isomeric purity. [b] In acetonitrile (100 mL). Irradiation was done at an ice-cold temperature. [c] Immediately after the reaction. GLC analysis on a 3-m tricresyl phosphate column (10% on Neopak 1A) at 40 °C. [d] Immediately after the reaction. GLC analysis on a 6-m dioctyl sebacate column (10% on Diasolid S) at 22 °C.

photoproduct except that the former has an additional fraction with an approximate molecular weight of 2000 in the gel permeation analysis and the presence of nitrogen (about 2.5% in weight) which can be easily detected by the characteristic absorptions at 1565 and 1640 cm^{-1} (–N=O). The polymeric products react with pyridine at room temperature and give a crystalline pyridine adduct ($C_3H_6O_3S \cdot C_5H_5N$, see the Experimental Section). In hot dimethyl sulfoxide the polymer is oxidatively cleaved.[8]

Olefinic Substrates Other Than Propylene

Other olefins were examined to see if the reactions are general. So far as we have examined, the formation of epoxides is largely dependent on the stability of the epoxides under the reaction conditions and polymeric products are always observed.

As mentioned earlier epoxides are generally not stable under the photochemical reaction conditions. Cyclohexene and 1-octene, for example, are consumed as well as sulfur dioxide and oxygen during irradiation to form polymeric products but the corresponding epoxides cannot be detected in the reaction mixtures. Both *trans*- and *cis*-2-butenes give mixtures of *trans*- and *cis*-2,3-epoxybutanes (trans rich, Table I). 2,3-Dimethyl-2-butene gives acetone apparently indicating some mechanism other than epoxidation is operating. Ethylene affords ethylene oxide and ethylene glycol diacetate can be isolated when ethylene is bubbled through a mixture of sulfur dioxide, oxygen, and acetic anhydride (as solvent) under irradiation.

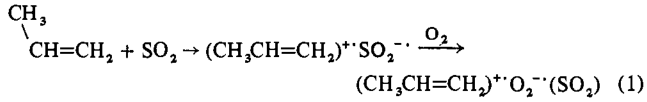
Most olefinic compounds are thermally oxidized at room temperature in the presence of potassium nitrite, sulfur dioxide, and oxygen in acetonitrile. For example, a mixture of *endo*- and *exo*-6-cyanonorborn-2-enes gives a mixture of *endo*- and *exo*-6-cyano-2,3-epoxynorbornanes. Cycloheptene gives cycloheptene oxide, while cyclohexene does not give the corresponding epoxide. 1-Octene gives 1,2-epoxyoctane with a small amount of heptanal. 2,3-Dimethyl-2-butene gives acetone. *trans*-2-Butene affords *trans*-2,3-epoxybutane stereospecifically but *cis*-2-butene gives a mixture of *trans*- and *cis*-epoxybutanes (Table I).

Reaction Mechanisms

A simple olefin like propylene is usually considered to be too electron poor to react with free singlet oxygen.[9] Since the reactivities of 2,3-dimethyl-2-butene and tetraphenylcyclopentadienone measured as oxygen absorption rate are not much different from that of propylene under our reaction conditions the possibility that singlet oxygen plays a significant role will be small.

The interaction of sulfur dioxide and olefins has been known to produce polysulfones[10] and the reaction is observed as a minor side reaction in the photochemical epoxidation reported here. The alternating copolymerization reaction is retarded by the presence of oxygen. The epoxidation reactions in the presence of sulfur dioxide neither can be initiated nor accelerated by added free-radical initiators.

Sulfur dioxide makes charge-transfer complexes with electron-donating molecules[11] and is known as an electron acceptor.[12] Likewise molecular oxygen can form charge-transfer complexes with electron-donating molecules[13] and is a well-known electron acceptor[14] (superoxide ion formation[15]). Since both the photochemical and the thermal reactions are controlled by the ionization potentials of additives and solvent polarity, it might be reasonable to assume the formation of some solvated radical ions and their important role in the epoxidation reactions. With the above information in mind the finding by Nagai et al.[16] that ion radicals can be formed in liquid sulfur dioxide between electron-donating olefins and molecular oxygen is important and pertinent to our present study. For example, Nagai et al.[16c] showed that cationic polymerization of styrene can be initiated by a termolecular complex oxygen–sulfur dioxide–olefin. Oxygen plays an essential role in generating the cation radicals which can be spectrophotometrically detected. Though propylene is a much poorer electron donor than the olefins used by Nagai, a similar mechanistic consideration might be reasonably applied to the present reaction system. Since the electron affinity of sulfur dioxide (0.2–0.3 eV) is larger than that of oxygen (0.15 eV), propylene should be complexed first with sulfur dioxide eventually to undergo electron transfer. The complexation could be construed as a step through which sulfur dioxide removes electrons from organic substrate.[17] Then the resulting sulfur dioxide radical anion may be oxidized by oxygen, the radical cation formation thus being accelerated.



$$CH_3CH{=}CH_2 + SO_2 \rightarrow (CH_3CH{=}CH_2)^{+\cdot}SO_2^{-\cdot} \xrightarrow{O_2} (CH_3CH{=}CH_2)^{+\cdot}O_2^{-\cdot}(SO_2) \quad (1)$$

The presence of any compound with low ionization potential would interfere with the electron-transfer process. This type of interaction among an olefin, oxygen, and sulfur dioxide can be easily understood in the photochemical epoxidation reaction. Sulfur dioxide can be a sensitizer and sulfur dioxide at an excited state (probably triplet) could be a strong electron acceptor. It should be relevant to mention that the highly efficient photoepoxidation reaction found by Shimizu and Bartlett[18] is sensitized by α-diketones which are electron acceptors.[19] We do not yet have a very good understanding on the role of the nitrite salts in the thermal epoxidation reaction. It should be pointed out, however, that the role of the salts can be catalytic because the amount of epoxide produced can reach a few times that of the salt used in the reaction. Though the general reaction patterns are quite alike in the photochemical and the thermal reactions, the mechanistic details could well be different between them (see below for an economical explanation).

---

(8) Alkyl sulfonates can be oxidized with dimethyl sulfoxide: Applequist, D. E.; McKenzie, L. F. *J. Org. Chem.* **1977**, *42*, 1251.

(9) Kopecky, K.; Reich, H. *Can. J. Chem.* **1965**, *43*, 2265.

(10) (a) Snow, R. D.; Frey, F. E. *Ind. Eng. Chem.* **1938**, *30*, 176. (b) Ivin, K. J.; Rose, J. B. *Adv. Macromol. Chem.* **1968**, *1*, 336.

(11) Complexation between sulfur dioxide and amines is a well-known example. See, e.g., *J. Am. Chem. Soc.* **1946**, *68*, 997.

(12) The electron affinity of sulfur dioxide is 0.2–0.3 eV. See: Briegleb, G. "Elektronen Donator Acceptor Komplexe"; Springer-Verlag: Berlin, 1961.

(13) Tsubomura, H; Mulliken, R. S. *J. Am. Chem. Soc.* **1960**, *82*, 5966.

(14) The electron affinity of oxygen is 0.15 eV. See the reference in ref 12.

(15) Wilshire, J.; Sawyer, D. T. *Acc. Chem. Res.*, **1979**, *12*, 105.

(16) (a) Tokura, N.; Nagai, T.; Sonoyama, Y. *Tetrahedron Lett.* **1965**, 1145. (b) Nagai, T.; Miyazaki, T.; Tokura, N. *Polym. Lett.* **1968**, *6*, 345. (c) Nagai, T.; Miyazaki, T.; Sonoyama, Y.; Tokura, N. *J. Polym. Sci., Part A-1* **1968**, *6*, 3087.

(17) Misilamani, D.; Rogic, M. M. *Tetrahedron Lett.* **1978**, 3785.

(18) Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 4193.

(19) Bartlett, P. D.; Becherer, *Tetrahedron Lett.* **1978**, 2983.

There seems to be no satisfactory reasoning to employ for the epoxide-forming (oxygen-atom transfer) step. Martin[20] reported in their continuing alkoxysulfurane studies that sulfinyl oxides can oxidize olefins to epoxides. Some sulfinyl oxide type species formed by the reaction between sulfur dioxide and oxygen ($O_2^{-}\cdot(SO_2)$ in reaction 1) may play an important role in the photoepoxidation reaction.[21] Sulfur trioxide should then be formed concurrently and immediately react with an olefin to give polymeric products. This idea of partitioning of two oxygen atoms to an olefin and sulfur dioxide can be applied to the thermal epoxidation reaction in the presence of sulfur dioxide and nitrite salts. In this case the formation of nitric oxide is reasonably expected[22] and the reaction of nitric oxide with molecular oxygen may produce some oxidizing species for both sulfur dioxide and an olefin. A support for this mechanistic sequence is the report by Michejda et al.[23] that mixtures of nitric oxide and molecular oxygen can epoxidize olefins though the resulting epoxides are mostly unstable under their reaction conditions. They propose that the nitrosoperoxy radical which eventually collapses to two nitrogen dioxide molecules in the absence of oxygen acceptors is the epoxidizing agent. The reactions of oxides of nitrogen are well known in the lead chamber process for sulfuric acid and the discussion of spin inversion on oxygen[24] could be spared here.

The lack of stereospecificity in the *cis*-2-butene reactions (both photochemical and thermal) may be partly aided by isomerization of the olefin by irradiation and sulfur dioxide. Any more elaborate discussion on stereochemistry, however, cannot be offered here and the details and scope of the epoxidation reactions must await further study.

Experimental Section

Infrared spectra were obtained on a Hitachi 295 instrument. The NMR spectra were recorded on a Hitachi R20 B spectrometer. Analytical, and some preparative, GLC work were done on a Shimazu 4CPT. Microanalyses, gel permeation analyses, and GC/MS analyses were performed by the Analytical Center of the Showa Denko Co. Matheson anhydrous sulfur dioxide and Kanto Chemicals reagent grade acetonitrile were used throughout the experiments.

Photochemical Reaction 1. Propylene (15 mL/min) and a mixture of sulfur dioxide (15 mL/min) and oxygen (10 mL/min) were bubbled through acetonitrile (200 mL) at an ice-cold temperature for 1 h. Then the flow rate of sulfur dioxide was reduced to 2.3 mL/min and the acetonitrile solution was irradiated with a 400-W medium-pressure mercury-arc lamp through Pyrex for 6 h. A small amount of a white solid was observed on the lampside wall of the reaction flask. The reaction mixture was analyzed by GLC on a 3-m dioctyl sebacate (10% on Diasolid S) column at 40 °C. The only volatile product observed was collected preparatively. The infrared, NMR, and mass spectra were identical with those of propylene oxide. The amount of propylene oxide formed in the reaction was 12 mmol. The reaction mixture was filtered to give a white solid (0.02 g). The solvent was removed from the filtrate on a rotary evaporator. A colorless viscous liquid (2.90 g) was obtained.

The white solid decomposed at 275 °C (Diffrential Scanning Calorimetry). The infrared spectrum of the solid (KBr) showed strong characteristic absorptions at 1300 and 1120 cm^{-1} ($-SO_2-$): NMR (Me_2SO-d_6) δ 1.59 (broad doublet, 3 H), 3.15–4.30 (m, 3 H). The solid was assigned to be poly(propylene sulfone).[3]

Anal. Calcd for $C_3H_6O_2S$: C, 33.96; H, 5.66; S, 30.19. Found: C, 33.59; H, 5.51; S, 30.11.

The viscous liquid product (1.29 g) was dissolved into a mixture of acetone and ethyl acetate (60/40) and the solution was chromatographed on a silica gel column (eluted with a mixture of acetone and ethyl acetate (90/10)). The viscous liquid thus chromatographed was dried over phosphorus pentoxide under vacuum. The amount of the recovered product was 0.86 g: IR (neat) 3000, 2950, 1460, 1360 (sulfonate), 1240, 1170 (sulfonate), 970, 940, 900, 820, 740, 690, 640, 580, 490; NMR (acetone-d_6) δ 1.0–1.8 (m, 3 H; a doublet at δ 1.55, J = 6.5 Hz), 3.5–4.8 (m, 3 H).

Anal. Calcd for $C_3H_6O_3S$: C, 29.49; H, 4.95; S, 26.25. Found: C, 31.18; H, 5.53; S, 23.54.

The dimethylformamide–tetrahydrofuran (50/50) solution of the nonvolatile product (chromatographed on a silica gel column) was analyzed by gel permeation chromatography on a Shodex GPC A-803 column. The main fraction of the product had an approximate molecular weight of 3000 with small UV absorption at 254 nm. The fractions with lower molecular weights and larger UV absorption were also present (see the GPC analysis of the thermal product).

Photochemical Reaction 2. A mixture of sulfur dioxide (4.89 g, 76.4 mmol) and propylene (0.95 g, 22.6 mmol) in acetonitrile (100 mL) was irradiated in a flask connected to an oxygen reservoir at 28 °C (a 400-W medium-pressure mercury-arc lamp, through Pyrex). The amount of oxygen absorbed during 5 h of irradiation was 5.90 mmol. The reaction mixture was analyzed by GLC on a 3-m dioctyl sebacate column (10% on Diasolid S) at 40 °C. The amount of propylene oxide observed was 1.6 mmol. The solvent was evaporated off from the reaction mixture on a rotary evaporator. A colorless viscous liquid was obtained (1.10 g).

The solvent dependence of the photochemical reaction and the effects of additives were studied by following the procedure of photochemical reaction 1. The use of a low-pressure mercury-arc lamp (160 W) or a halogen lamp (500 W) did not give propylene oxide in any significant amount.

Stability of Propylene Oxide under the Photochemical Reaction Conditions. A mixture of propylene oxide (0.48 g, 8.4 mmol), sulfur dioxide (1.93 g, 30 mmol), and oxygen-saturated acetonitrile (100 mL) was irradiated with a 400-W medium-pressure mercury-arc lamp through Pyrex at an ice-cold temperature for 5 h. The GLC analysis of the reaction mixture on a dioctyl sebacate column (10% on Diasolid S) at 40 °C showed that propylene oxide had been completely lost. The solvent was removed from the reaction mixture on a rotary evaporator. A colorless viscous liquid (0.83 g) remained. IR (neat) 3400 (broad), 2990, 2950, 2900, 1740, 1680, 1515, 1460, 1390, 1260 (shoulder, strong), 1200 (strong), 1040, 990, 930, 810,590 cm^{-1}; NMR ($CDCl_3$) δ 0.95–1.75 (broad multiplet, 3 H), 3.95–4.25 (m, 2 H), 4.50–4.75 (m, 1 H). The structure of the nonvolatile liquid is more like that of a sulfite[7] rather than a sulfonate.

Thermal Oxidation Reaction 1. Oxygen (8.57 mL/min) and propylene (6.66 mL/min) were bubbled through a mixture of sulfur dioxide(7.17 g, 112 mmol) and potassium nitrite(1.0 g, more than 85% pure) in acetonitrile for 5 h at 27 °C. The reaction mixture was analyzed by GLC on a 3-m dioctyl phthalate column at 40 °C. Only one volatile product was detected and it was collected preparatively. The infrared, NMR, and mass spectra of the product were identical with those of propylene oxide. The amount of propylene oxide formed in the reaction was 15.3 mmol. The amount of sulfur dioxide which was lost during the reaction was 49 mmol. The reaction mixture was filtered and the solvent was removed from the colorless filtrate by rotary evaporation. A viscous liquid was obtained (2.60 g). The elemental analysis of the liquid (C, 30.25; H, 4.91; N, 2.83) showed that about 35% of the weight was the propylene component (21 mmol). That the nitrogen is not entirely from the solvent which could not be removed from the product is evident since the use of acetone as solvent also formed a similar nonvolatile product (C, 34.96; H, 5.52; N, 1.39). A portion of the viscous liquid (0.72 g) obtained in the reaction in acetonitrile was dissolved into 10 mL of ethyl acetate. The solution was transferred to a silica gel column and eluted with a mixture of ethyl acetate and petroleum ether (90/10). A slightly pale yellow colored liquid thus obtained was dried over phosphorus pentoxide under vacuum. The infrared spectrum of the liquid (neat on KBr) showed absorptions at 3450 (broard), 3000, 2960, 2900, 1730, 1640, 1565, 1460, 1355 (strong, sulfonate), 1280, 1245, 1170 (strong, sulfonate), 1030, 980, 935, 820, 640, 580, 530, 490; NMR (acetone-d_6) δ 1.0–1.65 (m, 3 H; a doublet at 1.55 with J = ca. 7.0 Hz), 3.55–5.65 (m, 3 H).

The white solid which was filtered out from the reaction mixture was potassium sulfate; IR (KBr) 1110 (strong), 620 cm^{-1}.

The gel permeation analysis of the dimethylformamide–tetrahydrofuran (50/50) solution of the liquid product on a Shodex GPC A-803 column showed that the main component consisted of two fractions with approximate molecular weights of 2000 and 3000. The preparative gel permeation analysis of the chloroform soluble fraction showed that in addition to the main polymeric fractions with strong infrared absorptions at 1360 and 1170 cm^{-1} there were two lower molecular weight fractions with larger UV absorption at 254 nm. One is the fraction with molecular weight of ca. 200, which showed characteristic infrared absorptions at 1640 and 1560 cm^{-1} ($-N{=}O$). The other is the lowest molecular weight fraction (essentially hydrocarbons based on the infrared spectrum).

---

(20) Martin, L. D.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 3511.

(21) We do not know about the possibility of the formation of a cyclic sulfate under our present reaction conditions. Some cyclic sulfates can be quantitatively converted to the corresponding epoxides. See: Nishinaga, A.; Nakabayashi. S. *Chem. Lett.* **1978**, 913.

(22) Nitric oxide formation was observed by the reaction of ethylene with sodium nitrite in acetic acid at 50 °C. See: Tamura, M.; Yasui, A. *Kogyo Kagaku Zasshi* **1969**, *72*, 575.

(23) Michejda, C. J.; Campbell, D. H.; Sieh, D. H.; Koepke, S. R. In "Organic Free Radicals"; Pryor, W. A., Ed.; American Chemical Society: Washington, D.C., 1978; 292.

(24) (a) Barton, D. H. R.; Haynes, R. K.; Leclerc, G.; Magnus, P. D.; Menzies, I. D. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2055.

Both the photochemical and the thermal reaction mixtures did not contain peroxides in any significant amount as judged from the iodometric titrations.

Thermal Oxidation Reaction 2. Propylene (9.5 mL/min) and oxygen (10.7 mL/min) were bubbled through an acetonitrile solution (100 mL) of sulfur dioxide (3.60 g, 56.2 mmol) and potassium nitrite (0.548 g, ca. 85% pure, 5.47 mmol) at 26.0 °C. The formation of propylene oxide and the loss of sulfur dioxide were monitored by GLC analysis and the result is shown in Figure 1.

Thermal Oxidation Reaction 3. Potassium nitrite (1.0 g, 85% pure) was added to a mixture of sulfur dioxide (6.32 g, 98.6 mmol) and propylene (0.87 g, 20.7 mmol) in acetonitrile (100 mL) in a 300-mL flask connected to an oxygen reservoir. The reaction mixture was stirred with a magnetic stirrer at 23 °C for 8 h. The amount of oxygen absorbed during the reaction was 7.4 mmol. The reaction mixture was analyzed by GLC on a 3-m dioctyl sebacate column (10% on Diasolid S) at 40 °C. The amount of propylene oxide formed in the reaction was 5.95 mmol and the amount of sulfur dioxide reacted was 11.3 mmol. The amount of propylene which remained in the reaction mixture was 4.3 mmol. After filtration the solvent was removed from the reaction mixture. A viscous liquid (0.95 g) remained in the flask.

Reaction of the Nonvolatile Product with Pyridine. The viscous product (0.31 g) obtained from the thermal oxidation reaction was dissolved into pyridine (2 mL) at room temperature. Some solids precipitated over a month; the solution was filtered and washed with chloroform and then dried in a silica gel desiccator under vacuum. IR (KBr) 3400 (broad), 3050, 2980, 2940, 1635, 1595, 1450, 1200 (strong), 1030 (m), 790, 780, 750, 710, 680, 610, 570,545, 515; NMR (Me_2SO-d_6) δ 1.15 (d, 3 H, J = 7 Hz), 2.90–3.40 (m, 2 H), 4.72 (d, 1 H, J = 7 Hz), 7.85–9.22 (m, pyridine ring protons, 5 H).

Anal. Calcd for $C_3H_6O_3S{\cdot}C_5H_5N$: C 47.74; H, 5.50; N, 6.96; S, 15.93. Found: C, 47.42; H, 5.42; N, 6.85; S, 16.22.

Stability of Propylene Oxide under the Thermal Oxidation Conditions. Oxygen (7.7 mL/min) was bubbled through a stirred mixture of propylene oxide (1.68 g, 28.9 mmol), sulfur dioxide (6.75 g, 105 mmol), and potassium nitrite (1.0 g, 85% pure) in acetonitrile (200 mL) at 30 °C. After 6 h the reaction mixture was analyzed by GLC on a 3-m dioctyl sebacate column (10% on Diasolid S) at 40 °C. Most of the propylene oxide (92%) remained in the mixture. The amounts of sulfur dioxide and propylene oxide which were lost during the reaction were 10 mmol and 2.4 mmol, respectively, and were not significantly larger than those driven away by the oxygen stream. The reaction mixture was filtered and the solvent was removed from the filtrate by rotary evaporation. Only a small amount of a liquid (ca. 0.05 g) was obtained. The infrared spectrum (neat on KBr) showed strong characteristic absorptions at 1630 and 1280 cm^{-1} ($-ONO_2$). The NMR spectrum($CDCl_3$) showed a pair of methyl doublets at around δ 1.29 (J = 6.5 Hz).

Thermolysis of the Nonvolatile Product. The viscous liquid product (0.12 g) obtained in the photochemical oxidation reaction (chromatographed on a silica gel column) was placed in a glass container and heated under a nitrogen stream with a Bunsen burner. The gas evolved was absorbed in cold toluene. The GLC analysis of the toluene solution on a 3-m dioctyl sebacate column showed the presence of acetone (1.13 mmol per 1 g of the liquid), sulfur dioxide (2.16 mmol per 1 g of the liquid), and propylene (1.04 mmol per 1 g of the liquid). The formation of propylene and acetone was confirmed by the NMR spectrum of the benzene solution of the evolved gases.

The thermolysis of the liquid product obtained from the thermal oxidation reaction gave a similar result.

Acknowledgment. The author wishes to thank Mr. R. Ishioka for his encouragement during the study and Mr. T. Tsukamoto for technical assistance. The author is much indebted to Drs. R. Kurosawa and T. Ueshima for a gift of 6-cyanonorborn-2-ene.

Magnetic and Micellar Effects on Photoreactions. 1. ^{13}C Isotopic Enrichment of Dibenzyl Ketone via Photolysis in Aqueous Detergent Solution

Nicholas J. Turro,* Ming-Fea Chow, Chao-Jen Chung, and Bernhard Kraeutler[†]

Contribution from the Chemistry Department, Columbia University,
New York, New York 10027, and Laboratorium fur Organische Chemie, Eidgenossische
Technische Hochschule, Zurich, CH-8092, Switzerland. *Received October 6, 1980*

Abstract: The photolysis of dibenzyl ketone (DBK) in homogeneous organic solutions and in micelle-containing detergent solutions has been investigated from the standpoint of determining the extent and location of ^{13}C enrichment that occurs. In a series of experiments it is established that for incomplete conversions the residual, recovered DBK is enriched in ^{13}C relative to the initial unphotolyzed DBK. The efficiency of the $^{13}C/^{12}C$ separation is shown to be characterized by an isotope enrichment parameter, α, which is independent of the extent of conversion. A combination of mass spectrometry and nuclear magnetic resonance spectroscopy provides support for the primary location of the ^{13}C enrichment at C-1 (the carbonyl carbon) with a lesser but significant enrichment at C-2 (the methylene carbon). A very small but experimentally distinct enrichment of the aromatic rings is indicated by ^{13}C NMR analysis. An isomer of DBK, 1-phenyl-4′-methylacetophenone (PMAP) is formed as a minor product of photolysis in micellar solutions. PMAP, like the recovered, residual DBK, is found to be substantially enriched in ^{13}C relative to the starting DBK. The magnitude of α is found to be significantly influenced by the application of laboratory magnetic fields to the photolysis sample. The latter result, along with the unusually large magnitude of α, suggests that the mechanism involved in isotopic enrichment is not dominated by kinetic mass isotope effects but rather by nuclear magnetic moment and/or magnetic spin isotope effects.

Introduction

The photolysis of dibenzyl ketone (DBK) in homogeneous organic solvents has been shown to proceed via an initial homolytic α cleavage of the T_1 state, followed by decarbonylation and eventual coupling of benzyl radicals to yield 1,2-diphenylethane, DPE (eq 1).[1] A strong CIDNP spectrum is generated during the photolysis of DBK.[2] Theoretical analysis of these spectra leads to the conclusion that DPE is formed via free-radical combination and that some cage recombination of $C_6H_5CH_2\dot{C}O$ $\dot{C}H_2C_6H_5$ geminate radical pairs occurs. According to the radical pair theory of CIDNP,[3] when a cage reaction of a geminate pair

$$C_6H_5CH_2COCH_2C_6H_5 \xrightarrow{h\nu} S_1 \rightarrow T_1 \rightarrow$$
$$C_6H_5CH_2\dot{C}O + C_6H_5\dot{C}H_2 \rightarrow C_6H_5CH_2CH_2C_6H_5 + CO \quad (1)$$

---

* To whom correspondence should be addressed at Columbia University.

[†] Eidgenossische Technische Hochschule.

(1) (a) Quinkert, G.; Opitz, K.; Wiersdorf, W. W.; Weinlich, J. *Tetrahedron Lett.* **1963**, 1863. (b) Engel, P. S. *J. Am. Chem. Soc.* **1970**, *92*, 6074. (c) Robbins, W. K.; Eastman, R. H. *Ibid.* **1970**, *92*, 6076, 6077.

(2) (a) Langhals, H.; Fischer, H. *Chem. Ber.* **1978**, *111*, 543. (b) Blank, B.; Mennitt, P. G.; Fischer, H. *Proc. 23rd Int. Congr. Pure Appl. Chem.* **1971**, *4*, 1.

0002-7863/81/1503-3886$01.25/0