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KINETICS AND MECHANISM OF THE OXIDATION OF DIBENZOTHIOPHENE IN HYDROCARBON SOLUTION

OXIDATION BY AQUEOUS HYDROGEN PEROXIDE-ACETIC ACID MIXTURES

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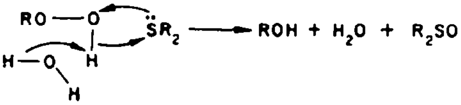
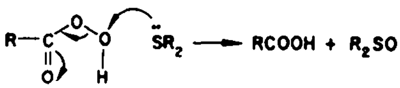
Abstract—The oxidation of white oil solutions of dibenzothiophene (DBT) by aqueous hydrogen peroxide–acetic acid solutions was studied kinetically at 50–100°. Under these conditions, the rate of DBT oxidation was found to be first order in acetic acid, second order in hydrogen peroxide, and inversely proportional to the water concentration. The activation energy between 50–100° in 64·5% acetic acid was 14 kcal/mole. We have also found that the monoxide is oxidized about 1·4 times faster than DBT. A mechanism consistent with the kinetic data has been postulated. The rate-determining step appears to be attack of a peracetic acid–hydrogen peroxide dimer on the sulfur atom of DBT.

THE oxidation of alkyl, alkenyl, aralkyl and aryl sulfides by hydrogen peroxide, hydroperoxides and peracids has been studied in detail.[1] Except for peracid systems, these reactions are subject to pronounced acid catalysis. Generally, the reactions are not influenced by free radical catalysts and inhibitors. In alcoholic or aqueous alcoholic solution, the reactions are first order with respect to both sulfide and peroxy compound.



Mechanistically, the reactions proceed by a one-step interaction of the sulfide with a peroxide–solvent complex in which a series of concerted electron displacements lead to hydrogen exchange and oxygen transfer. In the case of a peracid, intramolecular hydrogen bonding is possible and added protic species do not, in general, accelerate the oxidation step. In fact, it would appear that these reactions are inhibited by protic solvents. For example, in the oxidation of p,p'-dichlorobenzyl sulfide with perbenzoic acid, changing the solvent from isopropanol to toluene markedly increased the rate of oxidation.[2]



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[1] For reviews see (*a*) F. Challenger, *Aspects of the Organic Chemistry of Sulfur*, Chap. 1, p. 10. Academic Press, New York, N.Y. (1959). (*b*) E. E. Reid, *Organic Chemistry of Bivalent Sulfur* Vol. 2, Chap. 2, pp. 65–66. Chemical Publishing Co., New York, N.Y. (1960). (*c*) D. Barnard, L. Bateman and J. I. Cunneen, *Organic Sulfur Compounds*, Vol. I (Ed. by N. Kharasch) Chap. 21, pp. 229–247. Pergamon Press, New York, N.Y. (1961).

[2] C. G. Overberger and R. W. Cummins, *J. Amer. Chem. Soc.* 75, 4250 (1953).

In hydroperoxide oxidations, the use of an aprotic solvent produces changes which depend on the structure of the hydroperoxide, the sulfide and the solvent. In hydrocarbon media, the mechanism can be represented by Eq. 1. Under these conditions, the solvent is replaced by another hydroperoxide molecule and the reaction becomes termolecular. After the initial stages, the reaction becomes more complex since the sulfoxide complexes with the remaining hydroperoxide. The addition of an acid catalyst, e.g., acetic acid, causes the order of the reaction with respect to the hydroperoxide to revert to one.

In contrast to sulfides, little mechanistic work has been done on the oxidation of thiophenes to their corresponding monoxide and dioxide derivatives. Various thiophene monoxide and dioxide derivatives have been synthesized in a hydrogen peroxide–glacial acetic acid medium.[3,4] Only one kinetic study has been reported on the oxidation of dibenzothiophene and benzothiophene.[5] In benzene and benzene–acetic acid solutions, peracetic acid oxidation of thiophene derivatives adhered to second order kinetics. The rate constant for dibenzothiophene oxidations did not vary significantly with changes in the ratio of reactants, large changes in initial reactant concentration, and large changes in acetic acid concentration. When *tert*-butyl hydroperoxide was employed as the oxidizing agent, dibenzothiophene and benzothiophene were not readily oxidized and meaningful kinetic data could not be obtained. In view of these results and the lack of kinetic data on these compounds, we have carried out a detailed kinetic study on the oxidation of dibenzothiophene by hydrogen peroxide in white oil–aqueous acetic acid mixtures.

RESULTS AND DISCUSSION

Kinetic studies were carried out on dibenzothiophene (DBT) dissolved in a paraffinic white oil. Both DBT and its monoxide are soluble in the white oil at 100°. n-Hexadecane was added to the hydrocarbon phase as an internal GLC standard. The aqueous oxidizing agent was prepared by mixing the desired quantities of 30 wt% H_2O_2, glacial acetic acid and deionized water. The white oil and aqueous phases were separately heated to the desired reaction temperature before they were brought into reaction. Samples of the oil were withdrawn initially and as the run progressed and subsequently were analysed for the quantity of DBT remaining by gas chromatography. Reactions were carried out in a well-agitated flask. Experiments carried out at different rates of agitation showed that the reaction was not diffusion limited. It was also established that the hydrogen peroxide–acetic acid solutions are stable at 100° for at least 6 hr. Studies were conducted at different H_2O_2, acetic acid and water concentrations. The volume ratio of the aqueous and white oil phases was varied from 0·5 to 2·0. Temperatures from 50° to 100° were investigated. The mole ratios of the reagents to dibenzothiophene were such that consumption of the reagents was negligible over at least 50% of the reaction.

Figure 1 contains first order plots for the oxidation of DBT by H_2O_2 at 100° at various acetic acid concentrations. Since excess oxidizing agent was employed, the reactions are pseudo first order in DBT. The pseudo first order rate constants for each

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[3] H. Gilman and D. L. Esmay, *J. Amer. Chem. Soc.* **74**, 2021 (1952).

[4] J. L. Melles, *Rec. Trav. Chim.* **71**, 869 (1952).

[5] J. F. Ford and V. O. Young, *Preprints, Pet. Div. Amer. Chem. Soc.* **10**, No. 2, p. C-111, April 4–9, 1965.

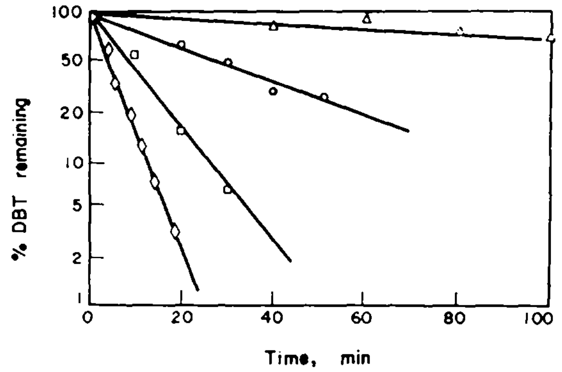


Fig. 1. Pseudo first order rate plots for the oxidation of dibenzothiophene by H_2O_2 at various acetic acid concentrations

Symbol	Volume % AcOH
△	8·6
○	43·0
□	64·5
◇	86·0

Table 1. Rate constants for the oxidation of dibenzothiophene as a function of acetic acid concentration at 100°[a]

Volume % AcOH in the aqueous phase	$k \times 10^3$, min^{-1}
8·6	3·2
43·0	25·5
64·5	94·1
86·0	346

[a] Using 5·14 g DBT, 100 ml white oil, 117 ml aq phase, and 5·6 moles H_2O_2 per mole DBT.

acetic acid concentration are summarized in Table 1. As shown, the rate of oxidation increased 100-fold as the volume of acetic acid was increased from 8·6 to 86%. In Fig. 2, the log of each rate constant is plotted as a function of the log of the initial mole ratio of acetic acid to water. A linear correlation was observed and the slope of the correlating line is unity. Linear and logarithmic plots of the rate constants against the concentration of either acetic acid or water did not yield a linear correlation. Therefore, the rate of oxidation is directly proportional to the acetic acid concentration and is inversely proportional to the water concentration. This correlation is consistent with the assumption that a steady state concentration of peracetic acid is involved in the rate determining step.

Oxidation experiments were next performed at 100° to determine the rate dependence on H_2O_2 concentration. The mole ratio of H_2O_2 to DBT was varied from 2·9 to 11·7 at different acetic acid concentrations. Figure 3 is a log–log plot of the apparent first order rate constants against the reagent phase H_2O_2 concentration (moles/l.) at three different acetic acid concentrations. The slope calculated for each line is 2. Therefore, the reaction is second order in H_2O_2.

Oxidation experiments were also conducted in 64·5 vol% acetic acid solutions to

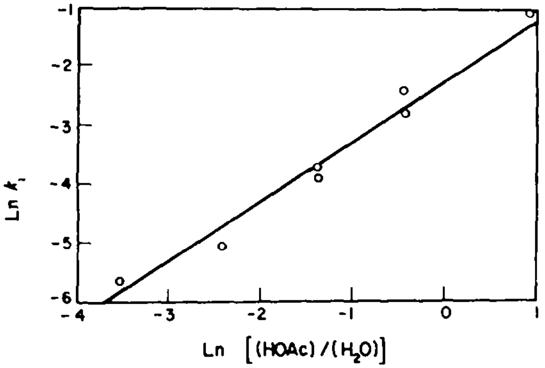


FIG. 2. Linear dependence of the rate of DBT oxidation on the mole ratio of acetic acid to water.

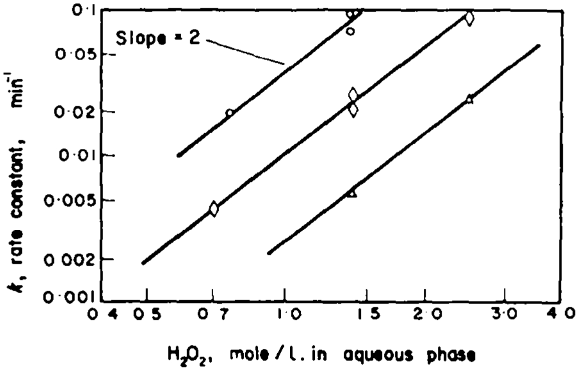


FIG. 3. Rate dependence of DBT oxidation on H_2O_2 concentration

Symbol	Volume % AcOH
△	21·0
◇	43·0
○	64·5

determine the activation energy for the oxidation of dibenzothiophene by H_2O_2 under these conditions. The reaction temperature was varied from 50° to 100°C. The rate constants for each temperature investigated are summarized in Table 2. Figure 4 is an Arrhenius plot of the apparent first order rate constants obtained. An activation energy of 14 kcal/g mole was calculated from the slope of the correlating line. Similar activation energies have been observed for the oxidation of organic sulfides to sulfoxides.[16]

The products of the oxidation of DBT by aqueous H_2O_2–acetic acid were isolated and subsequently analysed to determine the selectivity to dioxide. GC analyses showed that the product fraction was a mixture of dibenzothiophene monoxide and dibenzothiophene dioxide. A titration technique was employed to obtain quantitative data on the amount of monoxide produced. This technique is described in detail in the experimental. Product analyses were obtained at three different temperatures. The data in Table 3 show that, at 100°, the selectivity to sulfone is 100% after 120 min of reaction in solutions containing greater than 50 vol% acetic acid. The sulfone selectivity decreases as the temperature decreases. In the experiment using 100 ml

TABLE 2. RATE CONSTANTS FOR THE OXIDATION OF DBT AT 50–100° IN 64·5% AcOH[a]

Temp °C	$k \times 10^3$, min^{-1}
50	6·2, 6·5
75	34·0
85	48·6
100	94·1, 110

[a] Using 5·14 g DBT, 100 ml white oil, 75 ml AcOH, 25 ml water, and 16·6 ml 30% H_2O_2 (5·6 moles H_2O_2 per mole DBT).

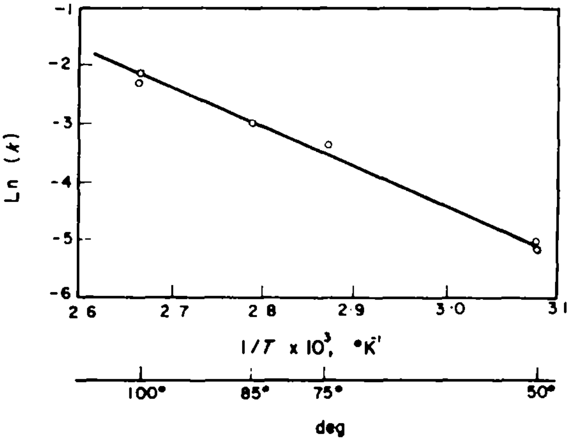


FIG. 4. Arrhenius plot for the oxidation of DBT in 64·5% acetic acid.

TABLE 3. DEPENDENCE OF MONOXIDE AND DIOXIDE SELECTIVITY ON REACTION TEMP

5·14 g dibenzothiophene–5 ml nC_{16}–100 ml white oil

Temp °C	30% H_2O_2, ml	AcOH ml	H_2O, ml	Reaction time, min	Mole/Mole DBT converted Sulfoxide	Sulfone
100	33·2	50	50	120	0·0	1·00
100	16·6	75	25	120	0·0	1·00
100	16·6	100	—	20	0·394	0·606
75	16·6	75	25	120	0·184	0·816
50	16·6	75	25	120	0·459	0·541

glacial acetic acid, which was terminated after only 20 min, the product was 39·4 mole % sulfoxide and 60·6 mole % sulfone. Therefore, the sulfoxide is the primary product.

An experiment was next performed in which 10·28 g DBT in 200 ml white oil were brought in to reaction with a solution containing 33·2 ml 30% H_2O_2, 150 ml acetic acid, and 50 ml water at 100°. Samples of the oil phase were periodically withdrawn and analysed for sulfoxide content. The sulfone yield was determined by difference. The moles of product/initial mole of DBT are plotted as a function of time in Fig. 5. Rate constants for the two oxidation reactions shown in Eq. 3 have been calculated from this data.

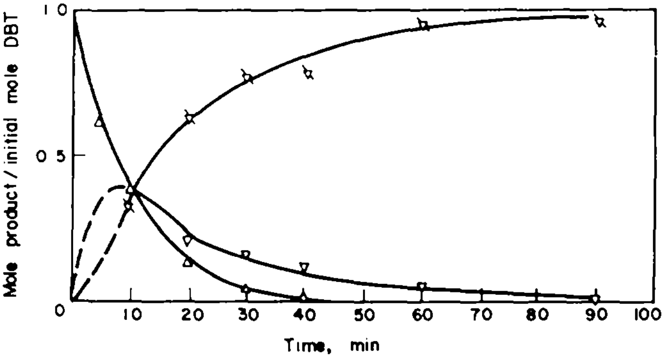
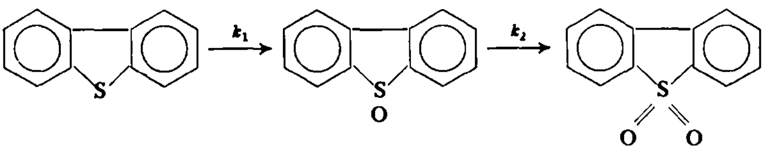


FIG. 5 Distribution of DBT monoxide and dioxide as a function of time at 100°

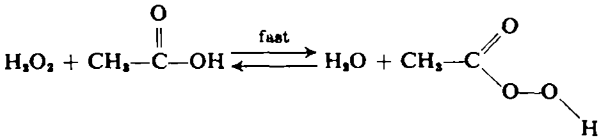
Symbol	Compound
△	DBT
▽	Monoxide
▽̸	Dioxide



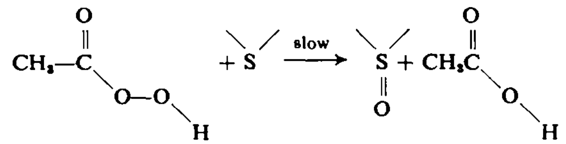
(3)

They are: $k_1 = 9{\cdot}40 \times 10^{-2}\,\mathrm{min}^{-1}$ and $k_2 = 13{\cdot}0 \times 10^{-2}\,\mathrm{min}^{-1}$. Therefore, the monoxide is oxidized about 1·4 times faster than DBT. This somewhat surprising result may be due to partial solubility of the sulfoxide in the aqueous phase. The rate constant for the oxidation of sulfoxide was not verified directly because we were unable to synthesize a sufficiently pure sample of sulfoxide even at 50°C. This is further evidence of the rapid rate with which DBT sulfoxide is oxidized.

Mechanistically, one can postulate several attacking species for the H_2O_2-acetic acid system. Among these are peracetic acid, protonated hydrogen peroxide $\mathrm{H{-}\overset{+}{\underset{H}{O}}{-}OH}$, and positively charged hydroxyl ion (HO^+). The last two intermediates may be discounted since we have found that sulfuric acid, which is a strong mineral acid, is a relatively poor catalyst in comparison to acetic acid. Let us assume, as the literature suggests,[1c] that peracetic acid is formed by fast reactions, that it is in equilibrium with H_2O_2, acetic acid and water, and that the rate-limiting reaction is a bimolecular attack of peracetic acid on the sulfur atom, i.e.,



$$H_2O_2 + CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH \xrightleftharpoons{\text{fast}} H_2O + CH_3{-}C\begin{matrix}\nearrow O \\ \searrow O{-}O{-}H\end{matrix} \quad (4)$$



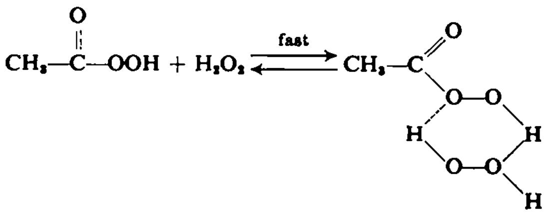
$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}O{-}H + \;\rangle S\langle\; \xrightarrow{\text{slow}} \;\rangle\underset{\underset{\displaystyle O}{\|}}{S}\langle\; + CH_3\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}H \quad (5)$$

This mechanism would lead to the following kinetic expression for the rate of DBT disappearance:

$$\text{rate} = \frac{-\mathrm{d}(\text{—S—})}{\mathrm{d}t} = \frac{k(\mathrm{H_2O_2})(\mathrm{CH_3COOH})}{(\mathrm{H_2O})}(\text{—S—}) \tag{6}$$

This expression predicts the observed dependence on acetic acid and water concentration, but does not satisfy the second order dependence on H_2O_2.

It has been reported, that hydroperoxides tend to exist in hydrogen-bonded dimer pairs.[6] If we postulate that the attacking species is a dimer composed of one molecule of peracetic acid and one molecule of H_2O_2, we can account for all of the kinetic data. A mechanistic path involving this dimeric oxidizing agent is outlined below.



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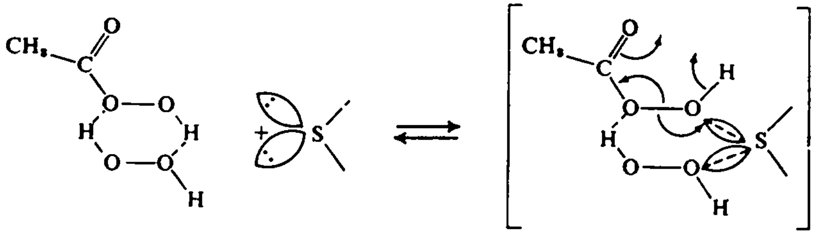

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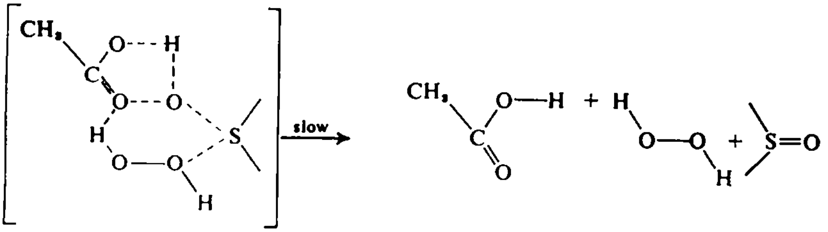

(9)

This mechanism leads to the following kinetic expression for the disappearance of dibenzothiophene:

$$\frac{-\mathrm{d}(\text{—S—})}{\mathrm{d}t} = \frac{k(\mathrm{H_2O_2})^2(\mathrm{CH_3COOH})}{(\mathrm{H_2O})}(\text{—S—}) \tag{10}$$

which is consistent with the observed rate dependence on peroxide concentration, acetic acid concentration and water concentration. This point is further emphasized by the data in Fig. 6 which contains a log-log plot of the pseudo first order rate constants as a function of $(H_2O_2)^2$ $(CH_3COOH)/(H_2O)$ at 100°. The slope of the correlating line is unity and this supports the above conclusions.

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[6] C. Walling and L. Heaton, *J. Amer. Chem. Soc.* **87**, 38 (1965).

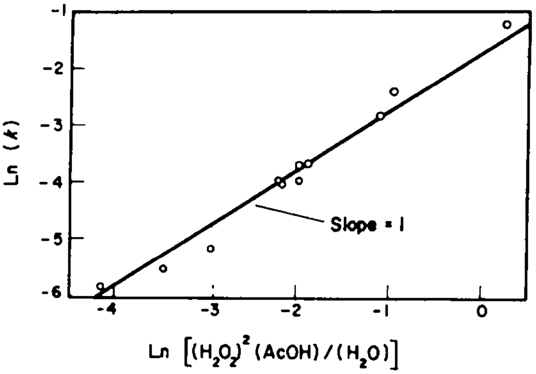

FIG. 6. Correlation of reaction rate with peroxide concentration, acetic acid concentration and water concentration.

EXPERIMENTAL

Materials. Dibenzothiophene (m.p. 96–98°) and olefin-free n-hexadecane were obtained from Matheson, Coleman, and Bell. Thirty wt% H_2O_2 and glacial AcOH were obtained from Fisher Scientific Company. White oil (b.p. 250° plus) was acquired from the Humble Oil and Refining Company. All materials were used as received. Dibenzothiophene monoxide and dibenzothiophene dioxide were synthesized according to the method of Gilman and Esmay.[3]

Preparation of reaction mixtures. White oil solutions of DBT were prepared by dissolving 5·14 g DBT and 5 ml n-hexadecane in 100 ml of the oil. This solution was heated in a temp controlled oil bath to the desired reaction temp. The aqueous reagent was prepared by adding the desired amounts of deionized water (<100 ppm as NaCl) and glacial AcOH to the reaction flask. This mixture was heated to the same reaction temp. The desired amount of 30 wt% H_2O_2 was added and the mixture again heated to the desired reaction temp. Each oxidation experiment was started by adding the oil solution of DBT to the reaction flask containing the H_2O_2aq phase. In general, this operation required about 2-3 sec.

The reaction flask (500 ml, 4-necked) was equipped with an appropriate mercury thermometer, a reflux condenser, mechanical stirrer and a self-sealing Neoprene cap. The reaction flask was continuously purged with N_2 which was introduced into the reaction flask through a hypodermic needle inserted through the Neoprene cap. The mechanical stirrer was operated at 1000 rev/min. Heat was supplied to the reaction flask by an electric mantle that was controlled by a Variac and Thermo-watch temp regulator. The temp of each reaction was maintained within ±0·5°.

Procedure for kinetic measurements. An aliquot was withdrawn from the oil phase prior to the initiation of each oxidation experiment. During the course of each run, stirring was interrupted, the phases were allowed to separate, and an aliquot was withdrawn from the oil phase by a hypodermic syringe that was inserted through the Neoprene cap. This operation usually required 10–15 sec. Stirring was then reinitiated. Eight to twelve 0·5 ml aliquots were withdrawn from the oil phase during the course of the run. Each aliquot was diluted with an equal volume of n-heptane prior to GC analysis.

The samples were analysed on an F and M 609 Flame Ionization Gas Chromatograph equipped with a disk integrator, a Minneapolis Honeywell recorder and a 2-ft silicone gum rubber column (10 wt% on Chromasorb P). The block and injection port temperatures were maintained at 300°. The column was maintained at 150–175°. The helium flow through the column was 100 ml/min when measured at room temp with a flow-meter. The amount of DBT remaining in the oil phase was determined by measuring its peak area relative to the n-hexadecane standard.[7]

Titration Technique for Determination of Dibenzothiophene Monoxide

The amount of dibenzothiophene monoxide produced was determined by a modified potentiometric

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[7] A. E. Messner, D. M. Rosie and P. A. Argabright, *Anal. Chem.* 31, 230 (1959).

titration technique that has previously been used for the estimation of aliphatic sulfoxides.[8] Approximately 0·1–0·2 g of the oxidation product was dissolved in 15 ml of glacial acetic acid and 125 ml of acetic anhydride. This solution was titrated potentiometrically with 0·1089N perchloric acid in p-dioxane solution using Calomel glass electrodes. LiBr (0·01N) was used as the bridge electrolyte. The perchloric acid had been previously standardized against potassium acid phthalate in AcOH–acetic anhydride solution. No interference was encountered from either dibenzothiophene or its dioxide. As a precautionary measure, the apparatus was shielded since occasional explosions were observed.

[8] D. C. Wimer, *Anal. Chem.* **30**, 2060 (1958).