[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Magnetic Measurements on 2,2′-Benzothiazyl Disulfide and bis-(9-Ethoxy-10-phenanthryl) Peroxide

BY HOWARD G. CUTFORTH[1] AND P. W. SELWOOD

The purpose of this investigation was to test the possible formation of free radicals in appreciable concentrations from diaryl disulfides and diaryl peroxides.

The existence of reversible dissociation to free radicals has been amply demonstrated for the C–C, N–N and Cl–Cl bonds.[2] It has also been shown that the following apparently do not dissociate: Si–Si, Ge–Ge, Sn–Sn, Pb–Pb and As–As.

There appears to be no direct evidence that diaryldisulfides dissociate. But some of these compounds show deviations from Beer's law, an ability to react with triarylmethyl radicals, and certain chemical properties which suggest free radical reaction mechanism.[3]

Most of the evidence for free radical formation from peroxides lies in the kinetic evidence from polymerization reactions.[4-6] Other evidences include deviations from Beer's law and subnormal molecular weights at the freezing point of benzene.[7,8] The photochemical dissociation of peroxides into free radicals has often been proposed.[9-11] But the existence of univalent oxygen can scarcely be considered as established.

The possible formation of free radicals by disulfides and peroxides is of interest because it would add to the very small list of elements (C, N, Cl) which definitely show reversible dissociation. There are also practical reasons for wanting to know whether free radical concentration can be appreciable in polymerization and vulcanization, and in cystine and related compounds and derivatives of biochemical interest.

Our choice of the two compounds: 2,2′-benzothiazyl disulfide and bis-(9-ethoxy-1-phenanthryl) peroxide was based on the following considerations: The disulfide is of importance in the processing of rubber, although the mechanism by which it operates is little understood. There is a possibility that this mechanism involves free radicals. Furthermore, the compound is reversibly thermochromatic; the color begins to appear in toluene solution at about 80°.

The peroxide was chosen for study because the phenanthryl groups appear to offer a good opportunity for resonance stabilization of an aroxy radical, and because molecular weight studies by Goldschmidt[8] indicate that dissociation occurs.

Experimental

Preparation of Materials.—The 2,2′-dibenzothiazyl disulfide was obtained from the United States Rubber Company through the courtesy of Dr. R. H. Ewart.

The bis-(9-ethoxy-10-phenanthryl) peroxide was prepared from crude phenanthrene in three steps. First, phenanthrenequinone was prepared as described by Adkins.[12] From the quinone, 9-ethoxy-10-phenanthrol was prepared by the method of Fourneau and Matti.[13] The phenanthrol with ethyl alcohol of crystallization had a melting range of 77–79° which agrees with 77° as reported by Japp.[14] bis-(9-Ethoxy-10-phenanthryl) peroxide was obtained by mild alkaline oxidation of the phenanthrol.[2] The peroxide was crystallized from a very small amount of benzene. The resulting sample decomposed at 138–139°, which agrees with 138° reported by Goldschmidt. *Anal.* C, found 83.88, calcd. 83.78; H, found 6.14, calcd. 6.07; O, found 9.98, calcd. 10.15. This is for the peroxide crystallized with two moles of benzene.

Benzene and toluene used as solvents in these studies were prepared by repeated extraction with concentrated sulfuric acid until the acid layer had no color. After the solvent was washed with distilled water, sodium bicarbonate solution, and again with distilled water, it was dried overnight over sodium. Finally it was distilled from sodium, and the middle third collected for use.

Density and Magnetic Susceptibility Measurements.—Density measurements and magnetic measurements on the Gouy balance have been described,[15,16] as has the treatment of data.[17]

The effect of light on the magnetic susceptibility of the diaryl peroxide was investigated on a very sensitive type of magnetic balance, using a horizontal suspension and a permanent magnet. This balance will be described in a forthcoming publication.

Preparations of Solutions.—The disulfide and peroxide solutions investigated on the Gouy balance were prepared in an apparatus shown in Fig. 1, as follows:

The apparatus was evacuated through E, with metallic sodium in A. This was allowed to stand overnight. The solute was introduced to chamber D, and the solvent was poured into bulb A. After the apparatus had been evacuated and sealed at E, the solvent was distilled from A to F by cooling F. Subsequently, the solvent was filtered through a sintered glass disc, the solute in D was dissolved, the solution was filtered through a second sintered glass disc, and the remainder of the apparatus was sealed off at I.

The peroxide dissolved quite readily, but the toluene had to be heated to get appreciable disulfide into solution. By tilting the apparatus the magnetic sample tube J and the expansion pycnometer K were filled to the correct height and were sealed off at their respective constrictions.

Photochemical Dissociation.—No further description is needed for the Gouy type of magnetic measurements, which were performed over a range of temperature. But the method

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(1) Present address: Rohm and Haas Company, Philadelphia, Pa.

(2) Waters, "The Chemistry of Free Radicals," Oxford University Press, Oxford, 1946.

(3) Schonberg, *Naturwissenschaften*, **21**, 561 (1933).

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(12) Oyster and Adkins,. THIS JOURNAL, **43**, 208 (1921).

(13) Fourneau and Matti, *Bull. soc. chim.*, **9**, 633 (1942).

(14) Japp, *Ber.*, **12**, 1306 (1879).

(15) Preckel and Selwood, THIS JOURNAL, **63**, 3397 (1941).

(16) Haller and Selwood, *ibid.*, **61**, 85 (1939).

(17) Selwood, "Magnetochemistry," Interscience Publishers, Inc. New York, N. Y., 1943, p. 124.

used for determining the effect of light on the magnetic susceptibility of peroxide solutions requires some further description.

A sample of peroxide was dissolved in benzene by mixing the two at room temperature. The magnetic sample tube and a 10-ml. weighing bottle were filled from a pipet. No special precautions were taken to exclude air because oxygen is reported to have little effect on peroxides of this type.[8] The solution so obtained was roughly analyzed for weight per cent. of peroxide.

The temperature of the suspended system during these observation was 25°. Changes of susceptibility were observed as linear displacements of the sample tube. These displacements were observed with a microscope and micrometer eyepiece. First, the sample was irradiated until a constant displacement was obtained. Then the system was left in the dark until a rest point was obtained.

Irradiation of the sample was furnished by two 200-watt tungsten lamps and by one mercury vapor lamp. However, as the sample tube was Pyrex glass, very little ultraviolet light reached the sample.

The time required for equilibrium in displacement was approximately thirty-five minutes. Observations were continued for thirty minutes after equilibrium had been reached.

Control experiments were made on pure benzene.

The quantity measured in the horizontal balance is the displacement, D. This displacement is perpendicular to the lines of flux in the magnetic field, and is caused by a change in magnetic susceptibility of the solution. Displacements could easily be read to 1 × 10^{-4} centimeter. This displacement was equivalent to a change of 4.68 × 10^{-10} unit of susceptibility.

Both in the light and in the dark we have the familiar relationship that $\chi_m = \chi_1 p_1 + \chi_2 p_2$, where χ_m is the susceptibility of the solution, χ_1 and χ_2, susceptibilities of the solute and solvent, and p_1 and p_2, weight fractions of solute and solvent. The temperature, fraction of solvent and susceptibility of solvent remain constant in light and dark; hence, the change in susceptibility on illumination of the sample

$$\Delta\chi = p_1(\chi_1^{\text{light}} - \chi_1^{\text{dark}})$$

but χ_1^{light} is equal to the algebraic sum of χ_1^{dark} and the susceptibility of any free radical which may be formed. Therefore,

$$\Delta\chi = p_1\chi_r$$

where χ_r is the susceptibility of the free radical. The molar paramagnetism for one unpaired electron spin at 25° is 1280 × 10^{-6}, so that the paramagnetic susceptibility for complete dissociation would be

$$2 \times 1280 \times 10^{-6}/M$$

where M is the molecular weight of the peroxide.

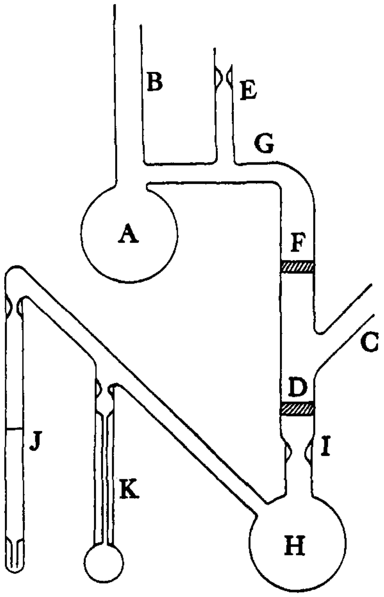

Fig. 1.—Apparatus for preparing peroxide and sulfide solutions and for filling pycnometer and magnetic sample tube.

The fraction of peroxide converted to free radicals is then

$$\alpha = \chi_r M/2 \times 1280 \times 10^{-6}$$

or, in terms of displacement in the horizontal magnetic balance

$$\begin{aligned}\alpha &= \Delta\chi M/2 \times 1280 \times 10^{-6} p \\ &= 1.8 \times 10^{-3}\, DM/p_1\end{aligned}$$

At a concentration of 3% peroxide, as little as 0.15% dissociation could be detected.

Results

Calibration of the Gouy magnetic balance was done with pure benzene and toluene, for which the susceptibilities at 25° were taken as −0.7065 × 10^{-6} and −0.7060 × 10^{-6}, respectively. The densities and susceptibilities at other temperatures as determined for this investigation are given in Table I. Table II shows the densities and susceptibilities of the diaryl peroxide dis-

TABLE I

DENSITIES AND MAGNETIC SUSCEPTIBILITIES OF BENZENE AND TOLUENE

Temp., °C.	Benzene d	Benzene $-\chi \times 10^6$	Toluene d	Toluene $-\chi \times 10^6$
10	0.8894 ± 0.0005	0.7072		
20	.8788	.7068		
25	.8734	.7065	0.8615	0.7060
30	.8680	.7064		
40	.8573	.7074		
50	.8465	.7084	.8283	.7068
60	.8356	.7094		
75			.8150	.7070
100			.7895	.7095
125			.7622	.7137
150			.7346	.7180

TABLE II

DENSITIES AND SUSCEPTIBILITIES OF BIS-(9-ETHOXY-10-PHENANTHRYL) PEROXIDE

Temp., °C.	Density of soln.	$\chi \times 10^6$ soln.	$\chi \times 10^6$ solute
Solvent, benzene; molality of peroxide, 0.0759			
20	0.8878	−0.7058	−0.677
30	.8773	− .7055	− .680
40	.8668	− .7059	− .663
Solvent, toluene; molality of peroxide, 0.00788			
20	.8675	− .7038	− .156
30	.8580	− .7044	− .215
40	.8487	− .7043	− .126
50	.8395	− .7051	− .239

solved in benzene and in toluene. The susceptibilities of the solutions are shown, in addition to the susceptibilities of the solute.

It will be noted that the solute is diamagnetic in all cases, and that it shows no temperature coefficient of susceptibility. The susceptibilities in toluene are numerically smaller than expected, but the low concentration of the solution renders the results in this solvent less accurate. We conclude that, under the conditions of these experiments, the diaryl peroxide is not dissociated to free radicals to an extent greater than 2%. This compares with a dissociation of 62% at room temperature reported by Goldschmidt.

TABLE III

EFFECT OF LIGHT ON THE SUSCEPTIBILITY OF BIS-(9-ETHOXY-10-PHENANTHRYL) PEROXIDE

Temperature 25°; molality of peroxide, 0.0556

Condition	Scale reading cm. $\times 10^4$ Pure benzene	Peroxide soln.
Illuminated	26.0	11.0
Dark	25.0	29.0
Illuminated	25.0	12.0

However, the effect of light on the peroxide gave a positive change of susceptibility. The results are shown in Table III. The deflection was in the direction of increasing algebraic susceptibility. If this change is due to dissociation, then the degree of dissociation under these conditions is 6%. The measurements on the Gouy balance are done with the sample in the dark. Presumably Goldschmidt's molecular weight determination was done with the sample not specially protected from the light. He reports that the dissociation proceeds slowly. There is, therefore, not necessarily any contradiction between the earlier results and those reported here.

We turn now to the results on the disulfide. These are given in Table IV.

TABLE IV

DENSITIES AND SUSCEPTIBILITIES AND DEGREE OF DISSOCIATION (α) OF 2,2′-BENZOTHIAZYL DISULFIDE

Solvent, toluene; molality of disulfide, 0.0148

Temp., °C.	Density soln.	$\chi \times 10^6$ soln.	$\chi \times 10^6$ solute	$\chi \times 10^6$ radical	α
25	0.8652	−0.7055	−0.6012	....	...
100	.7917	− .7077	− .3415	0.1996	0.032
125	.7672	− .7086	.3292	.8703	.151
150	.7427	− .7090	1.114	1.656	.305

Some comment is called for on the correction to be applied for the diamagnetism of the free radical. There are three ways of obtaining this correction. The first is to assume that no dissociation occurs at room temperature, hence the diamagnetism per gram of free radical is -0.6012×10^{-6}. Possibly this should be modified slightly because of the rupture of an S–S bond. The second method is by the use of Pascal's constants. These give a diamagnetism for the free radicals of -0.5400×10^{-6}. The third method is to measure the susceptibility of mercaptobenzothiazole and to correct for the additional hydrogen. The susceptibility of mercaptobenzothiazole at 25° was measured in toluene solution and found to be -0.5554×10^{-6}. Correction for the hydrogen atom gives a diamagnetism of the free radical of -0.5411×10^{-6}. This value was used in calculating the results shown in Table IV. Use of the larger diamagnetism derived from the disulfide at 25° would raise the degrees of dissociation somewhat.

However, the important conclusion is that the disulfide definitely forms free radicals. It is assumed that this occurs through dissociation across the sulfur–sulfur bond, but pending completion of ebullioscopic and other measurements now in progress it can scarcely be accepted as proved that dissociation produces the free radicals. Excitation to a triplet state would yield comparable magnetic results.

If dissociation actually occurs with the formation of thiol radicals then it is clear that the sulfur–sulfur bond breaks with considerably more difficulty than the carbon–carbon bond in hexaarylethanes. This result is, of course, not unexpected. The results reported here are scarcely accurate enough to make worthwhile a calculation of a heat of dissociation for the disulfide. But the heat is obviously greater than the 11 or 12 kilocalories per mole found for the hexaarylethanes.

The most interesting phase of these observations is the fact that free radicals must be formed in large amounts at temperatures used in the vulcanization of rubber with the disulfide. There is also raised the possibility that free radical concentration may be calculated for disulfides of biochemical interest at the temperature of the animal body.

It is a pleasure to acknowledge the support of the United States Rubber Company in connection with this work.

Summary

Magnetic measurements show that bis-(9-ethoxy-10-phenanthryl) peroxide does not dissociate appreciably in the dark in benzene or toluene solutions up to 50°. But exposure of the solu-

tion to light results in a magnetic change which could be interpreted as being due to appreciable dissociation.

A considerable degree of free radical formation is observed with 2,2'-dibenzothiazyl disulfide. The concentration of the thiol radicals in toluene has been measured up to 150°.

EVANSTON, ILLINOIS RECEIVED JUNE 20, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, SCHOOL OF MEDICINE, THE JOHNS HOPKINS UNIVERSITY]

Reaction Kinetics of Aliphatic Tertiary β-Chloroethylamines in Dilute Aqueous Solution. I. The Cyclization Process[1]

BY BARNETT COHEN, ERVIN R. VAN ARTSDALEN[2a] AND JOSEPH HARRIS[2b]

In contrast to ordinary alkyl halides, alkylamines possessing a halogen atom in the beta to omega position undergo a distinctive intramolecular transformation as the initial detectable reaction in polar solvents. The transformation yields halide ion and a more or less stable heterocyclic compound. In the case of the primary and secondary amines, the heterocycle may be either an imine or an imonium ion, depending on the *p*H of the solution. The tertiary amines can yield only the corresponding imonium ions.

The kinetics of the initial cyclization of a number of *primary* halogenated alkylamines has been reported.[3] The forward process of ring-formation was established as a unimolecular reaction, the rate of which was shown to be influenced by the length of the side-chain, by the substituents thereon, by the nature of the halogen and, especially, by the nature of the solvent.[4] The process is known to be reversible, but the kinetics of the reverse reaction seems not to have been studied, except for unsuccessful attempts[5] to determine an equilibrium constant in the β-bromoethylamine system. The failure was due to interference by side-reactions. It is known that in certain cases, at least, cyclic dimerization and linear polymerizations of the haloalkylamines can take place and become quantitatively important,[6] especially in concentrated solutions and at elevated temperatures.[7]

This report on a series of nine tertiary β-chloroethylamines supplements the older observations on the analogous primary amines. The compounds were of the general type $RR'NCH_2CH_2Cl$, where R and R' represent an alkyl group or a β-substituted ethyl group. Analytic evidence adduced here and elsewhere[6,8] shows that these compounds undergo the following initial reversible reaction

$$RR'NCH_2CH_2Cl \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} RR'\overset{+}{N}CH_2CH_2 + Cl^- \quad (1)$$

The first-order kinetics of the forward reaction can be established with relative ease because the reverse reaction is very much slower. The cyclic imonium ion is a reactive compound, but it possesses in many cases a fair degree of stability in water and can accumulate as reaction (1) proceeds.[6] The properties in solution and the reaction kinetics of the ethylenimonium ion will be considered in a subsequent report. In connection with the present discussion, it may be stated that the reaction kinetics indicates unequivocally that this ion is a singly charged cation.

Cyclization cannot occur when a proton is coördinated with the nitrogen atom of the amine. Consequently, in the case of these compounds, which are more or less weak bases, the rate of cyclization becomes a function of *p*H in solutions of moderate and low *p*H. In such cases, the observed rate constant, k_1', is defined by the relation

$$k_1' = \alpha k_1 = \frac{K_a' k_1}{K_a' + [H^+]}$$

where k_1 is the rate constant at *p*H conditions under which the ammonium ion is fully dissociated ($\alpha = 1$), and K_a' is the apparent dissociation constant of the ammonium ion as an acid.

It is obvious that the subsequent cyclization of a second and a third β-chloroethyl group, if present in these tertiary amines, is possible only after the antecedent heterocycle has been broken down,[9] *e. g.*, by hydrolysis. The rates of such subsequent cyclizations can best be determined by kinetic study of the corresponding chlorohydrins, as has been done in the case of N-methyl-bis-(β-chloroethyl)-amine and its chlorohydrin (see

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[1] The work described in this report was performed in major part under a contract recommended by the National Defense Research Committee, between the Office of Scientific Research and the Johns Hopkins University.

[2] (a) Present address: Department of Chemistry, Cornell University, Ithaca, N. Y. (b) The volunteer assistance of Marie E. Perkins is gratefully acknowledged.

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[4] Salomon, *Helv. Chim. Acta*, **16**, 1361 (1933); *Trans. Faraday Soc.*, **32**, 153 (1936).

[5] Freundlich and Neumann, *Z. physik. Chem.*, **87**, 69 (1914).

[6] Golumbic, Fruton and Bergmann, *J. Org. Chem.*, **11**, 518 (1946). This and the seven succeeding papers describe the chemical properties of the tertiary β-chloroethylamines.

[7] *Cf.* Lehmann, Thompson and Marvel, THIS JOURNAL, **55**, 1977 (1933).

[8] Hartley, Powell and Rydon, 1942, 1943. Unpublished data obtained in Great Britain; also *J. Chem. Soc.*, 513, 519, 527 (1947).

[9] This restriction need not apply to analogous secondary bis-β-halogenated amines which should permit double cyclization at a *p*H favorable to the ionization of the coördinated proton created by the initial cyclization.