SYNTHESIS AND STUDY OF DECOMPOSITION RATES OF SOME BIS FUROYL PEROXIDES AND SOME MIXED PEROXIDES

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# SYNTHESIS AND STUDY OF DECOMPOSITION RATES OF SOME BIS FUROYL PEROXIDES AND SOME MIXED PEROXIDES

presented by

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#### ABSTRACT

## SYNTHESIS AND STUDY OF DECOMPOSITION RATES OF SOME BIS FUROYL PEROXIDES AND SOME MIXED PEROXIDES

#### by Frederick Kabbe

The purpose of this study was to compare the decomposition rates and other properties of some bis and mixed furoyl, thenoyl, and benzoyl furoyl peroxides to assess identical substituent effects of different substituents on each other in the mixed peroxides. An additional objective of the investigation was to compare the effects of a furan ring system with the thiophene and benzene ring system.

The investigation required the preparation of (a) the furoyl acids and the corresponding acid chlorides, (b) the bis peroxides from the acid chlorides, (c) the mixed peroxides, and (d) the determination and comparison of the decomposition rates of the peroxides.

The general method of preparing the bis peroxides was to add an equivalent of pyridine to a stirred ice-cold ether solution containing equivalent amounts of hydrogen peroxide and the appropriate acid chloride. In an analogous manner the mixed peroxides were prepared from pyridine, a peracid and an acid chloride.

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The kinetic rates, activation energies, and entropies of activation were calculated by applying the least squares method to plots of the appropriate factors (a) log concentration (ml of thiosulfate or absorbance) vs time for k rates, and (b) log k vs 1/T for activation energy and entropy of activation.

A summary of peroxides prepared and their corresponding thermodynamic data is given in Table I below.

Table 1.

Compound (peroxide)	E <sub>a</sub> kcal. mole <sup>-1</sup>	∆s* (e.ū.)	k, 80 <sup>0</sup> min <sup>-1</sup> x 10 <sup>3</sup>	k/ko
Bis-(5-methvl-2-furovl)	20.6	-7.826	70	10
Bis-(5-chloro-2-furoyl)	24.0	-0.4722	19.0	3.0
Bis-(5-bromo-2-furoy1),	26.3	7.511	26	3.8
2-Furoyl-(5-chloro-2-furoyl)	26.6	8.670	11.2	1.6
Benzoyl-(2-thenoyl)	28.9	9.387	3.0	
Benzoyl-(2-furoyl)	29.8	13.30	4.6	
Bis-(2-furoyl)	30.6	16.62	7.0	1.0
Benzoyl-(5-bromo-2-furoyl)	30.6	16.21	6.7	
Bis-(3-furoyl)	32.0	17.62	2.4	
2-Furoyl-(5-bromo-2-furoyl)	33.0	23.80	10.5	1.5

Table 2. For comparison with Table I.

Compound (peroxide)	E <sub>a</sub> kcal. ∆S <sup>*</sup> mole <sup>-1</sup> (e.u.)	k, 80 <sup>0</sup> min-1 x 10 <sup>3</sup>
Bis-benzoyl (3)	30.2 4.5	2.59
Bis-(2-thenoyl) (5)	29.5 10.22	2.43

It was found that all substitutions on the bis-(furoyl) peroxides accelerate the rate of decomposition over that of the parent or unsubstituted compound.

Unsymmetrical peroxides formed from among benzoyl, furoyl, and thenoyl, groups have been found to have decomposition rates that are intermediate between the decomposition rates of the symmetrical peroxides which may be assumed to have supplied their mating acyl groups.

# SYNTHESIS AND STUDY OF DECOMPOSITION RATES OF SOME BIS FUROYL PEROXIDES AND SOME MIXED PEROXIDES

By (Cdl) Frederick Kabbe

A THESIS

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#### INTRODUCTION AND HISTORICAL

Organic peroxides are of both theoretical and practical importance. Many organic peroxides are formed spontaneously through the reaction of atmospheric oxygen with ethers, unsaturated hydrocarbons, and hydrocarbons having loosely bound hydrogens. The oxygen-oxygen bond has a bonding energy of 36 kilocalories and is relatively easily broken by thermal and radiant energy. When homolytic splitting occurs by rupture of the oxygen to oxygen bond, it results in the production of a very reactive free radical deficient in an electron. In recovering a pairing electron, it creates a new free radical which, in turn, demands an electron from its surrounding molecules. This process produces the familiar chain reaction and the free radical induced polymerization reaction.

A practical and reliable source of free radicals are the various diacyl peroxides. Benzoyl peroxide has been the most thoroughly investigated of the peroxides. Uninhibited thermal decomposition of benzoyl peroxide in various solvents give reaction orders from 0.5 to 2.0 (1), indicating that the uninhibited decomposition is complex. However, if the thermal decomposition is carried out in the presence of free radical scavengers (0.2M styrene, 2,4-dichlorostyrene,

1,4-diphenyl butadiene, or acrylonitrile), the kinetic plots follow the first order law. Since the effect of solvent upon the rate of decomposition is negligible, the half time of the uninhibited thermal decomposition of benzoyl peroxide at  $80^{\circ}$  is 23 minutes, that of the inhibited decomposition is 275 minutes at the same temperature.

A study of the relative effect of substituents upon the rates of decomposition of symmetrically substituted bis (benzoyl) peroxides has been made (2,3). The Hammett equation is fairly well obeyed for the meta and para substituted benzoyl peroxides. A rho ( $\rho$ ) value of -0.38 indicates that the spontaneous cleavage reaction is favored by high electron density at the reaction site. Therefore, electron releasing substituents such as alkyl groups should accelerate the process, whereas electron attractors, such as halogen and nitro substituents should retard the decomposition. The small value of the rho value indicates a relatively low susceptibility of this reaction to electronic effects.

The continuing interest in the chemistry of acyl peroxides is indicated by the 1964 A.C.S. symposium, "Development Stabilization and Uses of Organic Peroxides" (4). Guillett reported on the determination of decomposition rates of diacyl peroxides and presented clear evidence that the relative stabilities of aliphatic and aromatic peroxides are Alkyl-Peroxides > Aromatic acyl Peroxides > Aliphatic

acyl Peroxides. The aromatic and hetero aromatic acyl peroxides, such as benzoyl, furoyl, and thenoyl peroxides, apparently occupy a middle position in this stability series. This behavior may eventually add to their importance as initiators of free radical type polymerizations, which occupy an important place in present industrial chemistry. It was brought out repeatedly during the symposium that a careful study of the decomposition rates and mechanisms of as many of these compounds as is feasible should provide a sound basis for the choice of catalysts and optimum reaction temperatures for use in polymerization processes.

In these laboratories Schuetz and his collaborators (5,6,7,8) have extended the studies to the hetero aromatic systems, specifically derivatives of thiophene. The only peroxide of this series reported prior to the work of Schuetz and his co-workers was bis-(2-thenoyl) peroxide which had been prepared by Breitenbach and Karlinger (9) for use as an initiator in the free radical polymerization of styrene. These investigators synthesized the peroxide by the interaction of hydrogen peroxide and 2-thenoyl chloride in pyridine as a solvent. Schuetz and Teller (5) prepared a total of ten derivatives of bis-(2-thenoyl) peroxides, as well as the unsubstituted bis-(3-thenoyl) peroxide, using aqueous sodium peroxide which was allowed to react with the corresponding acid chloride dissolved in

a dry inert organic solvent such as toluene or cyclohexane. This procedure had been used by Price and Krebs (10) in the preparation of bis-(p-nitrobenzoyl) peroxide, and by Milas and McAlvey (11) in the preparation of bis-(2-furoy1) peroxide. The peroxides studied by Schuetz and Teller (5) were mainly derivatives of bis-(2-thenoyl) peroxide with substituents in the 5 position. Their work also included two sulfur heterocyclic peroxides having substituents (bromo and methyl respectively) in the 4 position. The decomposition reaction rates for these compounds were determined kinetically at three different temperatures in carbon tetrachloride as the reaction medium. Reaction rates were determined by iodometric titration of the unreacted peroxide. The inhibitor, 3,4-dichlorostyrene was used as a free radical scavenger, and under these conditions it was found that the first order rate law was followed for all the peroxide(s) studied except for the case of bis-(5-nitro-2-thenoyl) peroxide. Activation energies were estimated by plotting the logarithms of the rate constants against the reciprocal of the absolute temperature.

Schuetz and Gruen (12) extended the studies of the thiophene series to include (a) derivatives of substituted 3-thenoic acids, (b) peroxides comparable to ortho substituted benzoyl derivatives, and (c) a phenylated thenoyl peroxide. The thermal decomposition rates of the various substituted bis thenoyl peroxides were followed by a study

of their infrared spectra at 5.5 to 6.1 microns of carbon tetrachloride solutions containing 0.2 mole of purified styrene to inhibit induced decompositions. The typical "peroxide peak" occurred at approximately 5.7 microns with a slight shifting from compound to compound. Activation energies were determined from a plot of the logarithm of the rate constants determined, at three different reaction temperatures, against the reciprocal of the absolute temperature.

Using the formula,

 $s^{\#}/4.576 = \log k - 10.753 - \log T + E/4.576T$  (8) the entropies of activation were calculated for each peroxide.

The present investigation is an extension of the study of the peroxides to the bis furoyl peroxides and mixed unsymmetrical peroxides containing furoyl, benzoyl, and thenoyl entities. The bis furoyl peroxides were synthesized by the method of Silbert and Swern (13). A modification of the procedure was used to prepare the mixed peroxides. Essentially, an equivalent of an acid chloride was reacted with an equivalent of hydrogen peroxide or peracid in the presence of an equivalent of pyridine in ether solution at  $0^{\circ}$  to yield the desired peroxide. The kinetics of decomposition of peroxides were determined at several different temperatures.

#### EXPERIMENTAL

#### Chemical Reagents and Apparatus

The chloroform used in the determinations of the rates of decomposition of the bis and mixed heterocyclic peroxides was purified by washing it with small portions of concentrated sulfuric acid until no yellow color was observable in the acid layer. The chloroform layer was then washed with water to remove the remaining sulfuric acid and dried by the azeotropic distillation of the small residue of water which remained in the chloroform.

The styrene employed as a free radical scavenger in the kinetic studies was vacuum distilled and stored in the refrigerator in a brown bottle without inhibitor.

The thionyl chloride was purified by distillation from linseed oil according to the procedure recommended by Fieser (14).

The hydrogen peroxide was obtained from Baker Chemicals as analyzed 30%.

The ampules used in the kinetic determinations were made from Pyrex glass which had been heated overnight in concentrated sulfuric acid and then washed with water, ammonia, and again with water. The glass was then oven-dried at 120°.

The kinetic determinations were conducted in an oil bath controlled to a temperature variation of  $\pm 0.1^{\circ}$ .

All melting points were determined on a Kofler Hot Stage.

The Eastman furoyl chloride was distilled just prior to its use in preparing bis furoyl peroxide.

The pyridine was obtained from Eastman Company as spectro grade material.

The furoic acid was purchased from Eastman Company as their practical grade product. It was purified by recrystallization from water.

### Synthesis Leading to Bis Peroxides

#### Bis-(2-furoyl) Peroxide

The amount of peroxide available from commercial sodium peroxide is variable and the use of an excess of sodium peroxide in synthetic procedures reduces the yield of the organic peroxide obtained. Therefore, a mixture of pyridine and an analyzed solution of nominally 30% hydrogen peroxide was used as the source of the inorganic peroxide.

A magnetic stirrer and ice bath were provided for a 50 ml Erlenmeyer flask. The flask was charged with 0.8 g (0.006 mole) of freshly distilled 2-furoyl chloride, 0.32 ml of 30% hydrogen peroxide (0.003 moles), and 0.5 ml of pyridine (0.006 mole). The mixture was stirred at  $0^{\circ}$  for an hour. A small volume of 10% sodium carbonate was added

and stirring was continued five minutes after which the aqueous layer was removed by pipetting. A second portion of 10% sodium carbonate solution was added and the ether layer was allowed to evaporate from the surface of the aqueous layer resulting in the precipitation of a light, yellow, crystalline product. This was recovered by filtration, washed with cold water, and air dried. The yield of crude product was 0.478 g (0.00215 mole, 70%) melting at 81-84<sup>°</sup>.

The crude bis-(2-furoyl) peroxide was dissolved in dichloromethane, centrifuged, and decanted to remove a small amount of greenish-yellow colored, oily material. The decantate from this oily material was reduced in volume, diluted with pentane, cooled in a dry ice-acetone bath, and then centrifuged. The solvent was decanted and the residue was washed with pentane. The residue was dried under vacuum at room temperature, initially at a water aspirator pressure and then for an hour in a mechanically pumped vacuum oven. The product was nearly colorless and melted at 86-87°. Literature value (11) 86-87°.

Equivalent weight calculated for  $C_{10}H_6O_6$ : 111. Equivalent weight found: 110.3

## 3-Furoic Acid

3-Furoic acid was prepared from furan tetracarboxylic acid by a modification of the procedure of Reichstein et al. (15). The furan tetracarboxylic acid was obtained

from sodium diethyl oxalacetate by the method of Sutter (16).

A 88 g quantity (0.42 mole) of sodium diethyl oxalacetate was suspended in 300 ml of chloroform and cooled in an icesalt bath. To the well-shaken oxalacetate solution was added slowly 30 g (10 ml) (0.17 mole) of bromine in 30 ml of chloroform during 30 minutes. The bromine was promptly absorbed and a fluid, gluey suspension resulted. The finely divided sodium bromide could not be removed by filtration or centrifugation. The mixture was concentrated on a steam bath, cooled, and diluted with water. The ether solution was washed several times with water, then with saturated sodium chloride solution, and dried with sodium sulfate. The ether and chloroform were removed under vacuum to obtain 45 g (0.12 mole) of tetraethyl dioxalsuccinate as a glassy material which slowly crystallized during a period of a week.

A 30 g quantity (0.08 mole) of the ester was added in a small amount to cold concentrated sulfuric acid and stirred until it had dissolved. The mixture was then heated to  $50^{\circ}$ , held at this temperature for five minutes, cooled, and then poured onto well-stirred, crushed ice. An oily wax appeared. The mixture was transferred to a separatory funnel and the aqueous layer was extracted twice with ether. The combined ether extracts were washed initially three times with water, then three times with cold sodium hydroxide, and finally with water until the washings and the ether layer were

colorless. The ether layer was separated, dried with sodium sulfate, and the ether was removed under reduced pressure. The residue which was set aside in the refrigerator to crystallize yielded 19 g of tetraethyl furantetracarboxylate (0.053 mole) which melted at  $32-3^{\circ}$ . Literature value (15)  $34.5^{\circ}$ .

A 15 g quantity (0.046 mole) of the tetraethyl furantetracarboxylate was hydrolyzed by refluxing it for six hours in a mixture of 60 ml of water and 60 ml of concentrated hydrochloric acid. The solution was concentrated to half its volume, then 30 ml of concentrated hydrochloric acid and 30 ml of glacial acetic acid were added and the mixture was again refluxed for six hours and then concentrated to half its original volume. To insure complete hydrolysis this procedure was repeated twice, each time with the addition of 30 ml of concentrated hydrochloric acid and 30 ml of glacial acetic acid. The solution was then evaporated to dryness to yield 11.5 g of gray, crude furantetracarboxylic acid. An 8 g quantity (0.33 mole) of the crude furantetracarboxylic acid was mixed with 0.8 g of copper powder and 10 ml of quinoline in a distillation flask equipped with a gas inlet tube to admit a nitrogen gas stream nearly to the bottom of the flask. The flask was carefully heated with a free Bunsen flame while a moderate stream of nitrogen was passed through the system.

In one preparation a gas suspension of dry, smokey particles was swept from the system with a very small recovery of product. In a second preparation, a sodium bicarbonate solution was used to trap the acid product. The alkaline material in the trap was adidified to Congo red indicator with hydrochloric acid and set aside in the refrigerator overnight. The acid was recovered by filtration, washed, and dried to obtain 2.6 g (0.023 mole, 70%) of 3-furoic acid which melted at 121-122°. Literature value (15) 122-123°.

#### 3-Furoyl Chloride

A mixture of a 1.0 g (0.0096 mole) quantity of 3-furoic acid and 2 ml (0.025 mole) of thionyl chloride was refluxed for 18 hours over a micro hot plate. After the end of the reaction period, three 2 ml portions of <u>n</u>-hexane were added to the reaction mixture and removed by vacuum distillation from the residue of 2-furoyl chloride. This effectively removed the excess thionyl chloride. The yield was 0.58 g (0.0056 mole, 47%) of crude 3-furoyl chloride which was used without further purification in the synthesis of bis-(3-furoyl) peroxide.

## <u>Bis-(3-furoyl)</u> Peroxide

Into a 25 ml round bottom flask was placed 0.58 g (0.0045 mole) crude 3-furoyl chloride and 0.22 ml (0.002 mole) of 30% hydrogen peroxide. The mixture was magnetically stirred and cooled by immersion in an ice-water bath. A solution of 0.32 ml (0.004 mole) of pyridine in 4 ml of ether was gradually added to the reaction flask and the mixture was stirred at  $0^{\circ}$  for an additional hour. The lower layer was removed with a micropipet, and the upper (ether) layer was treated successively with two 10 ml water washes, two 10 ml 10% sodium carbonate washes, and finally with two 10 ml water washes. Each aqueous wash layer was removed with a micropipet. A 10 ml volume of water was added to the resulting ether solution and the ether was completely removed by evaporation to leave the water insoluble bis-(3-furoyl) peroxide floating on the surface of the water. The water was removed by a micropipet and the crystals were washed twice with cold water, dried at room temperature first under aspirator vacuum, and more completely in a mechanically pumped oven.

The dried crystals were transferred to a Pyrex ignition tube and dissolved in the minimum amount of dichloromethane and centrifuged. This procedure deposited a small amount of greenish-yellow, oily material which was insoluble in dichloromethane, ether, or water but was soluble in acetone. The solution was decanted, and the residue was rinsed with dichloromethane and the washings were added to the decanted solution. The volume of the solution was reduced by directing a stream of nitrogen or natural gas over the surface of the solution. Pentane was added until cloudiness appeared, at which point the mixture was cooled to dry ice-acetone temperature, immediately centrifuged,

and the pentane decanted. The residue was rinsed with pentane, cooled to dry ice-acetone temperature, again centrifuged, and the liquid phase was decanted. Additional solvent was removed from the crystals by forcing a micropipet to the bottom of the vessel and pumping the mixture as dry as possible. The pentane and ether were removed at room temperature by evaporation, initially at water pump pressure and then in a mechanically pumped vacuum oven. The product 0.38 g (0.003 mole, 52%) melted at 74.0-75°.

Equivalent weight calculated for  $C_{10}H_8O_8$ : 111 Equivalent weight found: 109.5 Calculated for  $C_{10}H_8O_8$ : C, 54.1; H, 2.70 Found: C, 53.69; H, 2.57

#### 5-Bromo-2-furoic Acid

This acid was prepared by the method of Whittaker (17). A solution of 21 g (0.13 mole) of bromine in 15 ml of chloroform was added gradually to a solution of 11.4 g (0.1 mole) of 2-furoic acid in 50 ml of chloroform and the mixture was refluxed for three hours, during which time large amounts of hydrogen bromide were evolved. A yellow crystalline crust formed and did not redissolve in the hot chloroform. After the early stages of the refluxing very little bromine was lost from the dark red solution. In the later stages the mixture became largely a reddish-yellow solid. At the end of the reaction period, the chloroform was removed under reduced pressure, the residue was dissolved with 80 ml of 6<u>N</u> sodium hydroxide solution, and 9 g (0.037 mole) of barium chloride and 1 g of charcoal were added. The mixture was boiled, filtered, and the charcoal treatment repeated until an almost colorless solution resulted. The solution was made acidic to Congo red indicator with dilute hydrochloric acid heated to dissolve the crystals which had precipitated, and then set aside to crystallize. The cold solution was filtered to recover 4 g (0.002 mole, 21%) of pure 5-bromo-2furoic acid which melted at 190-191°. Literature value (19)  $190^{\circ}$ .

#### 5-Bromo-2-furoyl Chloride

A mixture of 1.02 g (0.0053 mole) of 5-bromo-2-furoic acid and 2 ml (3.30 g) (0.03 mole) thionyl chloride was placed in a 25 ml round bottom flask and heated at its reflux temperature for six hours with a micro hot plate.

After cooling the reaction mixture, the excess thionyl chloride was removed by vacuum distilling three successive 10 ml portions of <u>n</u>-hexane from the residual 5-bromo-2-furoyl chloride (18). Without transferring, and without further purification, the crude 5-bromo-2-furoyl chloride was used directly in the preparation of the bis-(5-bromo-2-furyoyl) peroxide.

#### Bis-(5-bromo-2-furoyl) Peroxide

A flask containing 1.0 g (0.005 mole) crude 5-bromo-2-furoyl chloride was placed in an ice bath and provided with a magnetic stirrer. A 20 ml volume of ether containing 0.35

ml of 30% hydrogen peroxide (0.003 mole) was added to the reaction mixture followed by the dropwise addition of a solution of 0.6 ml (0.007 mole) of pyridine in 4 ml of ether. The reaction mixture was stirred for an hour at  $0^{\circ}$  during which time a light yellow, finely divided suspension developed. On the addition of 10 ml of water, the ether layer cleared and the water layer acquired the suspended product which was recovered by filtration. The ether layer of the filtrate was separated, the ether removed, and the product thus obtained was combined with the product recovered by filtration of the water suspension. The crude product was 0.68 g (0.0018, 75%) which melted at 113-114.5°.

The crude bis-(5-bromo-2-furoyl) peroxide was dissolved in a minimum quantity of acetone, precipitated with water, centrifuged, and dried at room temperature in a vacuum oven. The purified product melted at 116-116.5<sup>°</sup>.

Equivalent weight calculated for  $C_{10}H_4Br_2O_6$ : 190 Equivalent weight found: 195 Calculated for  $C_{10}H_4Br_2O_6$ : C, 31.6; H, 1.05; Br, 42.1 Found: C, 31.45; H, 1.14; Br, 41.9.

### 5-Chloro-2-furoic Acid

The experimental procedure of Sheppard, Winslow, and Johnson (20) was used to prepare this acid. A 64 g (0.5 mole) quantity of methyl-2-furoate was heated to 145<sup>°</sup> and dry chlorine gas passed through the ester until a weight gain of 17 g (0.5 mole of chlorine) was obtained which corresponded

to the substitution of one hydrogen by chlorine. The resulting viscous liquid was slowly added to excess alcoholic sodium hydroxide with cooling. The sparingly soluble sodium salt of the desired acid was recovered by filtration, redissolved in water, acidified with hydrochloric acid to obtain the free acid which was recovered by filtration. There was 31 g (0.214 mole, 43%) of dry crude product. The 5-chloro-2-furoic acid was recrystallized from benzene yielding colorless, shiny plates which melted at 182-182.5°; Literature value (19) 179-180°.

# 5-Chloro-2-furoyl Chloride

A 0.85 g quantity (0.0058 mole) of 5-chloro-2-furoic acid and 2 ml (0.028 mole) of thionyl chloride was added to a 25 ml round bottom flask fitted with a reflux condenser. The reaction mixture was heated to its reflux temperature for 9 hours with a micro hot plate. The excess thionyl chloride was removed by adding two successive 5 ml portions of <u>n</u>-hexane and distilling the mixture at water aspirator pressure. The high boiling residue was not distilled but was used directly to prepare the bis-(5-chloro-2-furoyl) peroxide.

## <u>Bis-(5-chloro-2-furoyl)</u> Peroxide

A flask containing 0.86 g (0.005 mole) crude 5-chloro-2-furoyl chloride was placed in an ice bath and provided with a magnetic stirrer. A 10 ml volume of ether, 0.4 ml (0.0036 mole) of 30% hydrogen peroxide, and 0.5 ml (0.006 mole) of pyridine were added and the mixture was then stirred for an hour at  $0^{\circ}$  during which a light yellow suspension developed in the ether layer. The addition of water to the reaction mixture cleared the ether layer and the suspension appeared in the water layer. This mixture was set aside overnight in a refrigerator to allow the material to become crystalline. The reaction mixture was filtered on a glass sintered crucible and the product was washed on the filter with water. The ether layer of the filtrate was separated and the ether removed. The residual product was washed with water and combined with the solid from the reaction mixture. The combined solids were dried under vacuum at room temperature to obtain 0.59 (0.002 mole, 70%) of crude peroxide having a melting point of 110-111.5°.

The crude peroxide was dissolved in a minimum amount of acetone and reprecipitated by adding water. The pure peroxide was recovered by filtration and dried under vacuum at room temperature. It melted at 111.5<sup>°</sup>.

Equivalent weight calculated for  $C_{10}H_8Cl_{22}O_6$ : 149.5 Equivalent weight found: 145.5 Calculated for  $C_{10}H_8Cl_2O_6$ : C, 41.2; H, 1.38; Cl, 24.37 Found: C, 40.85; H, 1.29; Cl, 24.18.

### Methyl-5-chloromethyl Furoate

Methyl-5-chloromethyl furoate was prepared by the method of Andrisano (21). A dry stream of hydrogen chloride gas was passed through an unheated, stirred mixture of 250 ml of

chloroform, 126 g (1.00 mole) of methyl-2-furoate, 43 g (1.43 moles as formaldehyde) of paraformaldehyde and 36 g (0.261 mole) of anhydrous zinc chloride. The reaction temperature rose to  $35^{\circ}$  during the first part of the reaction period. After about four hours of reaction, the temperature dropped to room temperature and the mixture was poured into water. The chloroform layer was separated, washed with water, and dried over anhydrous sodium sulfate. The solvent was removed by distillation at atmospheric pressure and the residue of crude product was distilled under reduced pressure to obtain 83.5 g (0.60 mole, 60%) of pure product which boiled at 137/20 mm Hg. Literature value (21) 136/17 Hg.

Note: This compound has a vesicant action; very small amounts and very short contact times lead to persistent itching and burning sensations on areas of the skin exposed to the material. Also, some red itching blotches appeared on areas of the body which were remote (e.g. shoulder) from the point of contact with the material.

#### 5-Methyl-2-furoic Acid

A mixture of 270 ml of glacial acetic acid, 30 ml of water, and 80 ml of zinc was heated to its reflux temperature. Then an 83.5 g (0.4 mole) quantity of methyl-chloromethyl-2-furoate was gradually added to the reaction mixture during a period of 30 minutes, after which the mixture was refluxed for two hours and then poured into water. The oily product was separated and dried over anhydrous sodium

sulfate. Distillation of the crude product yielded 30 g (0.21 mole, 45%) of pure methyl-5-methyl-2-furoate which boiled at 215-216°. Literature value (21) 216°.

The 30 g (0.21 mole) quantity of methyl-5-methyl-2furoate was hydrolyzed by refluxing it with 50 ml of 20%sodium hydroxide for two hours. The hydrolyzate was acidified with hydrochloric acid to Congo red and filtered to obtain 3 g (0.024 mole, 11%) of pure acid, which melted at 109.7-110°. Literature value (21) 108-109°.

Note: 5-Methyl-2-furoic acid is very soluble in water. It is probable that a much higher yield would have been obtained if the product solution had been evaporated to dryness and extracted with ether and the acid then recovered from the ether. Alternatively, the acid could have been obtained by sublimation from the dried residue.

#### Bis-(5-methyl-2-furoyl) Peroxide

A 1 g (0.007 mole) quantity of crude 5-methyl-2furoyl chloride and 10 ml of ether were placed in a 25 ml round bottom flask. The solution was magnetically stirred and cooled by immersion in an ice bath. A 0.34 ml volume of 30% hydrogen peroxide (0.003 mole) was added to the reaction mixture followed by the gradual addition of a solution containing 0.55 ml (0.007 mole) of pyridine in 4 ml of ether. The mixture was stirred an additional hour at  $0^{\circ}$ to complete the reaction. At the end of the reaction period, the lower layer was removed with a micropipet and the upper (ether) layer was washed successively with 10 ml portions each of water, 10% sodium carbonate, and water.

A 10 ml volume of water was added to the mixture and the ether was removed by directing a jet of nitrogen over the surface of the solution. The water-insoluble peroxide crystallized from the solution on the surface of the water. The water was removed from the solid with a micropipet. The crystalline peroxide product was dried at room temperature, initially at water aspirator pressure and finally in a mechanically pumped vacuum oven.

The dry crude product was dissolved in ether, centrifuged to remove a dense, yellow, oily material which was insoluble in ether, dichloromethane, or water. The ether solution was decanted and was reduced in volume by a jet of nitrogen blown across its surface. The concentrated solution was cooled in a dry ice-acetone mixture, centrifuged, and the solvent was decanted. The residue was rinsed with pentane, again cooled, centrifuged, and the pentane decanted. The pure peroxide was freed of pentane solvent in a vacuum oven at room temperature at water aspirator pressure ( $\sim$  20 mm Hg). The yield of product was 0.245 g (0.002 mole, 25% overall from the acid) which melted at  $66-68^{\circ}$ .

Equivalent weight calculated for  $C_{12}H_{10}O_6$ : 125 Found: 122-125 Calculated for  $C_{12}H_{10}O_6$ : C, 57.6; H, 4.0 Found: C, 57.79; H, 3.95.

# <u>Procedure for Kinetic Determination</u> of the Bis Peroxides

The thermal rates of the furan peroxide decompositions were determined by measuring the rate of disappearance of the infrared peak of the peroxide group at 5.7 microns. Shea (7) and Teller (6) used carbon tetrachloride as the solvent for their kinetic studies of the thiophene peroxides. Since the solubilities of some of the furan bis peroxides were not large enough in carbon tetrachloride to allow kinetic determinations to be made, chloroform was used in preparing the peroxide solutions.

A 0.01 to  $0.015\underline{M}$  solution of each of the bis peroxides was prepared in a specially purified chloroform which was  $0.2\underline{M}$  in styrene. It was unnecessary to know the exact concentrations of the solutions used since the infrared peak values were directly proportional to the log of the peroxide concentrations in the absorbance range from 0.2 to 0.65.

The peroxide samples used in the rate studies were sealed in double ended ampules. These were made by progressively drawing specially cleaned 6 mm Pyrex tubing to give ampules about 0.3 ml in volume. The ampules remained connected together until filled with the peroxide solution.

A set of the ampules was flushed with purified nitrogen. The nitrogen inlet was clamped off, and the open end of the group of ampules was dipped into the peroxide solution. The clamped rubber tubing on the gas inlet end was squeezed

enough to expell one ampule volume of nitrogen and then released. When the sample had flowed into the lower ampule, its upper constriction was fused and the rest of the ampules were removed. The filled ampule was then placed closed end downward in a dry ice-acetone bath and the open end sealed. Then the lower sealed end of the rest of the ampule group was cut off and the lower ampule filled as above. The procedure was repeated until a sufficient number of ampules were filled. The filled ampules for a given bis peroxide decomposition rate determination were prepared at one time and stored in a refrigerator at  $4^{\circ}$  until needed.

When the ampules of several peroxides whose decomposition rates at a specific temperature were to be measured, were ready, they were strung together with heavy cotton cords. Each peroxide sample occupied the same relative position on each cord and was identifiable by its position on the cord. The prepared cords of samples were dropped, simultaneously into an oil bath maintained at a given temperature  $\pm 0.1^{\circ}$ . At specific time intervals a set of samples was withdrawn, quenched and washed in petroleum ether, and stored in the refrigerator until infrared measurements were made.

When enough samples were available, the strings of ampules were set out in chronological order on a bench. One end of each ampule was cut off and the open end inserted into the inlet of an infrared cell. When the closed end of the

ampule was cut off, the sample flowed into the cell. Five or more individual measurements were made on a single sample by running through the immediate peak area, resetging the machine, shifting the paper slightly sideways, and repeating the peak measurement.

Other samples of the same peroxide were run on the same sheet by setting the cylinder at different stops and resetting the machine to run through the 5.7 micron region. In this way all pertinent data for a given peroxide was accumulated on a single sheet. This procedure was used with each peroxide at each specific temperature in the rate determinations.

# Synthesis Leading to Unsymmetrical Mixed Peroxides

## Perbenzoic Acid

Perbenzoic acid was prepared by a modification of the procedure reported by Vogel (22).

A 2.6 g (0.11 mole) quantity of sodium was placed in a dry flask and covered with 50 ml of absolute methanol. The reaction flask was cooled to moderate the reaction. The resulting sodium methoxide solution was cooled to  $-5^{\circ}$  by immersion in an ice-salt bath. To the rapidly stirred sodium methoxide solution was added a solution of 25 g (0.10 mole) of freshly recrystallized benzoyl peroxide in 100 ml of chloroform. The addition of the organic peroxide was made at a rate such that the temperature of the reaction mixture
did not rise above 0°. The reaction mixture was stirred for five minutes to complete the reaction and then it was transferred to a separatory funnel and extracted with 250 ml of ice and water. The chloroform layer was separated and the aqueous layer was extracted twice with 50 ml portions of cold chloroform. The chloroform extracts were discarded. The aqueous solution was made acidic to Congo red with 6N sulfuric acid and extracted with three 50 ml portions of cold ether. The combined ether extracts were dried with sodium sulfate, and concentrated by evaporation at room temperature under reduced pressure. The concentrated solution was stored in the freezing compartment of a refrigerator at  $-20^{\circ}$ . When needed for a preparation, the solution was analyzed for perbenzoic acid and an appropriate volume taken for the reaction. Analysis showed a production of 7.4 g (0.053 mole,  $\sim 60\%$ ) of perbenzoic acid.

# Benzoyl-(2-furoyl) Peroxide

A 16 ml volume of perbenzoic acid solution in ether (equivalent to 1 g (0.008 mole)) of perbenzoic acid was placed in a flask and held at  $0^{\circ}$  by immersion in an ice bath. A 0.95 g (0.0075 mole) of 2-furoyl chloride in ether was added to the perbenzoic solution. Then 0.6 g (0.0075 mole) of pyridine in ether was slowly added to the well-stirred reaction mixture. The reaction was completed by stirring the mixture for an additional hour. The ether solution was then washed successively with water, 10% sodium carbonate solution,

and saturated sodium chloride, and dried with anhydrous sodium sulfate. The ether solution was concentrated at room temperature under reduced pressure. Pentane was added until the solution became slightly cloudy and then it was cooled to dry ice temperature to crystallize from solution 0.90 g (0.004 mole, 51%) of crude crystalline peroxide. This was recovered by filtration. It had the physical properties, m.p.  $59-60^{\circ}$ ; equivalent weight 133 (theoretical 116). Successive crystallization of the peroxide from methanol, methanol-water, ether-pentane, methanol, methanolwater, yielded pure product melting at  $61-61.5^{\circ}$ , with an equivalent weight of 121.

Calculated for C12H8O5: C, 62.2; H, 3.45

Found: C, 62.23; H, 3.49.

#### <u>Benzoyl-(5-bromo-2-furoyl)</u> Peroxide

A volume of the ether solution of perbenzoic acid containing 0.46 g (0.00033 mole) of perbenzoic acid and 0.7 g (0.00033 mole) of 5-bromo-2-furoyl chloride were mixed and cooled to 0<sup>°</sup> by immersion in an ice bath. A 0.4 g (0.0052 mole) quantity of pyridine in ether was added dropwise to the magnetically stirred reaction mixture. After stirring for one hour to complete the reaction, the ether solution was washed first with water, then with 10% sodium carbonate, and finally with saturated sodium chloride and then dried with anhydrous sodium sulfate. Pentane was added to the dry solution to produce a slight cloudiness in the ether solution. Crystallizing the peroxide from solution at dry ice temperature yielded 0.50 g (0.0016 mole, 50%) of product, melting at 68-69°, equivalent weight 159 (theory 155.5).

Calculated for C<sub>12</sub>H<sub>7</sub>O<sub>5</sub>Br: C, 46.3; H, 2.25; Br, 25.7 Found: C, 46.44; H, 2.29; Br, 25.5.

### <u>Benzoyl-(2-thenoyl)</u> Peroxide

A 16 ml volume of the ether solution of perbenzoic acid (equivalent to 1 g, 0.0072 mole) of perbenzoic acid was mixed with 1.06 g (0.0072 mole) of 2-thenoyl chloride in a flask and cooled by immersion in an ice bath. An 0.8 g (0.01 mole) guantity of pyridine in ether was added dropwise to the magnetically stirred reaction mixture. To complete the reaction, the mixture was stirred for an additional hour. The reaction mixture was then washed successively with water, 10% sodium carbonate, and saturated sodium chloride, and dried with anhydrous sodium sulfate. Pentane was added to the ether solutions until a slight cloudiness appeared and the mixture was then cooled by immersion in a dry iceacetone bath to crystallize from solution 1.20 g (0.005 mole, 67%) of crude peroxide which melted at  $89-93^{\circ}$ . Recrystallization of the crude product from methanol at -20° (refrigerator) yielded a material melting at 93.5-94° with an equivalent weight of 120 (theory 124).

Calculated for C<sub>12</sub>H<sub>8</sub>O<sub>4</sub>S: C, 58.15; H, 3.22; S, 12.90 Found: C, 58.02; H, 3.12; S, 12.90.

#### Furoperacid

The method of Milas and McAlvey (11) was used to synthesize this acid. To a solution of 180 ml of anhydrous ether containing 6 g (0.03 mole) of bis-2-furoyl peroxide and cooled in an ice-salt mixture to  $-5^{\circ}$  was added slowly under vigorous magnetic stirring 24 ml of ice-cold anhydrous methanol containing sodium methoxide equivalent to 0.66 g (0.028 mole) of sodium. After adding the heterocyclic peroxide the reaction mixture was stirred for eight minutes and then poured into 60 ml of ice and water and shaken. The non-aqueous layer was removed and the aqueous layer was separated and extracted, first with two 60 ml portions of cold chloroform and then with 60 ml of cold ether. The chloroform and ether extracts were discarded. A 60 ml volume of ether was added to the aqueous layer and the mixture was made acidic to Congo red with 6N sulfuric acid. The ether layer was separated and saved. The aqueous solution was extracted twice with 60 ml portions of cold ether. The ether extracts were combined, dried with anhydrous sodium sulfate, and concentrated at room temperature under reduced pressure. The ether solution was stored in a freezer until used in the synthesis of the mixed peroxides. The solution was analyzed for peroxide content prior to its use in the synthesis of the mixed peroxides.

## 2-Furoyl-(5-bromo-2-furoyl) Peroxide

A 0.42 g (0.002 mole) quantity of 5-bromo-2-furoic chloride was mixed in ether solution with an excess of

perfuroic acid and the mixture was cooled to  $0^{\circ}$  by immersion in an ice bath. A slight excess of pyridine in ether was added dropwise to the magnetically stirred reaction mixture. After stirring for an hour to complete the reaction, the mixture was washed successively with water, 10%sodium carbonate, and saturated sodium chloride, and then dried with sodium sulfate. Pentane was added and the solution was cooled to dry ice temperature to crystallize from solution 0.35 g (0.0012 mole, 75%) of crude peroxide. The peroxide was recovered by filtration and recrystallization from ether-pentane to yield, 0.23 g (0.00077 mole) of crystalline powder which melted at 82.5-83.5°, equivalent weight 145 (theory 150).

Calculated for C<sub>10</sub>H<sub>4</sub>Br<sub>2</sub>O<sub>8</sub>: C, 39.9; H, 1.66; Br, 26.6 Found: C, 40.19; H, 1.86; Br, 26.44

#### 2-Furoyl-5-chloro-2-furoyl Peroxide

The furcy1-5-chloro-furcy1 peroxide was prepared by the reaction of 5-chloro-furcy1 chloride with perfurcic acid in the presence of pyridine. A 0.83 g (0.0050 mole) quantity of 5-chloro-furcy1 chloride was placed in a round-bottom flask fitted with a magnetic stirrer, and to this was added 15 ml of anhydrous ether and the mixture was cooled in an ice bath to  $0^{\circ}$ . To this solution a 0.75 g (0.0050 mole) quantity of perfurcic acid in 25 ml of anhydrous ether at  $0^{\circ}$  was added. This was then maintained at  $0^{\circ}$  while adding a 0.45 ml (0.0056 mole) quantity of pyridine in 5 ml of anhydrous ether dropwise while stirring. The reaction mixture was then stirred at  $0^{\circ}$  for one hour. The mixture was then washed twice with water, once with sodium carbonate solution, again with water, and filtered through anhydrous sodium sulfate. Pentane was then added and the mixture cooled in a dry ice-acetone bath and the crystals separated and collected centrifugally. The crystals were recrystallized from ether-pentane with cooling. The yield of the product was 1.0 grams (0.0035 mole, 66%) which melted at  $91-92^{\circ}$ .

Calculateted for C<sub>10</sub>H<sub>5</sub>O<sub>6</sub>Cl: C, 46.81; H, 1.97; Cl, 13.82 Found: C, 46.78; H, 1.93; Cl, 13.94.

# <u>Preparation and Standardization of</u> <u>Sodium Thiosulfate Solution</u>

A 2.50 (0.01 mole) quantity of reagent grade sodium thiosulfate was dissolved in 2 liters of previously boiled distilled water, and 0.2 g of sodium carbonate was added as a stabilizer. This solution was standardized against a standard iodine solution which had been standardized initially against a standard solution prepared from primary standard arsenic trioxide.

### Standardization of Thiosulfate Solution

The volume ratio of iodine solution to arsenite solution was determined by the usual analytical procedure. However,

in the standardization of the thiosulfate solution by the iodine solution, it was necessary to use the same amount of acetone (10 ml) as was used in the titration of the peroxide samples and to use a timed sequence of operations in order to obtain meaningful and duplicable peroxide equivalent weights. If the acetone and the timed sequence were not used, low peroxide equivalent weights resulted.

With the use of acetone in the standardization of the thiosulfate solution, the equivalent weights of the purified benzoyl peroxide and of bis furoyl peroxide were acceptable and reproducible.

Benzoyl peroxide equivalent weight Calculated for  $C_{14}H_{10}O_4$ : 121 Found: 121.1-121.3 Bis-2-furoyl peroxide equivalent weight Calculated for  $C_{10}H_6O_6$ : 111 Found: 110.4-111

The calculation of the normality of the thiosulfate is given by the following equation,

$$N = \frac{q - As_2 O_3}{ml - As_2 O_2} \times \frac{4 - eq - AS_2 O_3}{MW - g - AS_2 O_3} \times \frac{ml - As_2 O_3}{ml - I_2} \times \frac{ml - I_2}{ml - S_2 O_3} \times \frac{1 - eq - I_2}{1 - eq - I_2} \times \frac{1 - eq - I_2}{1 -$$

Since the reliability of the equivalent weight of pure benzoyl peroxide was proven, pure benzoyl peroxide was used as a primary standard when it became necessary to replenish the supply of thiosulfate solution.

## Equivalent Weight Determinations of the Organic Peroxides

The equivalent weights of the peroxides were determined by a modification of the potassium iodide-thiosulfate procedure using a starch-iodide endpoint. Since the peroxides were insoluble in aqueous media, it was necessary to dissolve the peroxide in an organic solvent which is miscible with a water solution of potassium iodide. The addition of saturated potassium iodide solution to an acetone solution of the peroxides resulted in an immediate release of an equivalent amount of iodine. The iodine was immediately titrated to a starch endpoint.

In a typical peroxide equivalent weight analysis, a 0.0145 g quantity (3.8 x  $10^{-5}$  moles) of bis-(5-bromo-2-furoyl) peroxide was dissolved in 10 ml of acetone, 2 ml of saturated potassium iodide solution added, and the solution swirled. The solution was diluted with 25 ml of water, starch indicator was added, and the solution was immediately titrated to a starch endpoint. The equivalent weight of the peroxide was calculated from the equation,

eq wt =  $\frac{q \text{ peroxide}}{m1 \cdot S_2 Q_3^{-}} \times \frac{1000 \cdot m1 \cdot S_2 Q_3^{-}}{eq \cdot S_2 Q_3^{-}} \times \frac{1 \cdot eq \cdot S_2 Q_3^{-}}{1 \cdot eq \cdot peroxide}$ <u>Kinetics of the Unsymmetrical</u> <u>Mixed Peroxides</u>

Double ended ampules of approximately 0.4 ml volume were drawn from specially cleaned 6 mm Pyrex tubing.

Five or six ampules were drawn in one continuous string, flushed with nitrogen and then were sealed off in groups of two. At the time of filling, the pairs of ampules were cut into separate ampules, filled, and sealed at room temperature.

Samples of equal volumes were measured by means of small pipets prepared from 3 mm Pyrex tubing. A small diameter tip was made by drawing the glass sufficiently so that the tip would slip inside the small opening of an ampule. A graduation mark was scratched on the tube to indicate the desired volume. Control of sample level was obtained by attaching a small syringe to the top of the pipet with a short section of rubber tubing. It was possible to duplicate samples within two or three milligrams using the same pipet.

The filled ampules were handled in the oil bath in the same way that the symmetrical bis peroxides had been. After the ampules were quenched and washed in petroleum ether, the sample was discharged into a 125 ml Erlenmeyer flask and the ampule flushed with one ml of methanol. Two ml of methanol were used to rinse down the sides of the Erlenmeyer flask. Then one ml of saturated potassium iodide solution was added and the solution thoroughly mixed. Very rapid and complete reaction occurred between the potassium iodide and the peroxide of the sample. The sample was immediately titrated with a thiosulfate

solution containing about 1.00 g of sodium thiosulfate per 4 liters of solution prepared with previously boiled water. The titration endpoint was taken as the disappearance of the yellow iodine color or the yellow starch color.

Titration volumes were plotted directly upon the log scale of semilog paper versus time plotted linearly on the abscissa.

Subjecting this data to a least squares calculation yielded the slope of the best curve. Multiplying the slope of the curve by 2.303 gave the k rate value.

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Applying the least squares method of the plot of log k versus 1/T yielded the slope and the intercept of the best curve (24). The activation energy was found by multiplying the slope by 2.303 R. Since log s is the intercept of the plot, its value may be substituted in the equation,

$$\Delta S^* = R \ln s - R \ln \frac{e k' T}{h}$$

to calculate the entropy of activation. In this equation k' is Boltzmann's constant and h is Planck's constant.

A summary of the thermodynamic data is found in Table XIV in the appendix.

# Attempted Synthesis of the 2-Difluoro-methyl and 2-Trimethyl Derivatives of Thiophene and Furan

About twenty months were spent in attempting to produce the desired fluoro compounds by the procedure of Sheppard et al. (23) by the reaction of phenyl-sulfur trifluoride with the appropriate aldehydes or acids. Gas chromatography of processed micro-reaction mixtures indicated the production of small yields (< 20%) was produced from the aldehydes of the difluoromethyl compounds and practically none (certainly < 1%) of the trifluoro compounds was produced from the acids. Gas chromatography showed only the formation of some anhydride from the acids when an attempt was made to synthesize the trifluoro compounds. All attempts to run any of the reactions in glass ended in disaster and no product was recovered.

It was intended to convert the fluoro compounds to the corresponding 2-substituted acids, then to the acid chlorides, and finally to the bis-(5-di-or-tri-fluoro-methyl) peroxides. The decomposition rates of these peroxides were then to be compared with the decomposition rates of the other peroxides prepared in this study.

Since difluoro thiophene was produced in the larger yield and was the more stable of all compounds whose synthesis was attempted, and since a similar procedure was used for all the compounds, the synthetic and investigative procedures that were used are described in terms of the attempted synthesis and recovery of difluoromethyl thiophene. A 0.221 g (0.0013 moles) quantity of phenyl sulfur trifluoride and 0.140g (0.0013 mole) of thenal were heat sealed in a polyethylene capsule made from  $\frac{1}{4}$  inch polyethylene tubing. (All transfers were made with polyethylene pipets which had been drawn from  $\frac{1}{4}$  inch polyethylene tubing.) Any given capsule was placed in an oven held at a given temperature  $< 65^{\circ}$  and for times < 10 hours. There was little weight loss during the reaction (< 2 mg). At the end of the reaction period, the capsule was cooled, cut open, and the contents diluted with about 1 ml of ether. The cold ether solution was washed repeatedly by jetting sodium carbonate solution through the sample solution. The sample was further processed in one of two ways:

1. The aqueous solution was removed as completely as possible by micropipet and the ether solution dried with saturated sodium chloride followed by anhydrous sodium sulfate. The dried ether solution and ether rinsings were combined in a tared vial and the solution was stored at -20 until the solution was gas chromatographed.

2. Alternatively, the polyethylene capsule was immersed in a dry ice-acetone mixture to freeze out the aqueous sodium carbonate solution. Then the ether and ether rinsings were combined in a tared vial and stored at -20 until gas chromatographed.

A 0.05 ml volume sample was injected into the gas chromatograph from a Hamilton microsyringe. Reaction mixtures

produced new peaks which occurred at elution times that were unique to the starting aldehyde. The peak areas were measured by weighting cardboard cut outs of the pertinent peaks. An estimate of yields was then calculated by comparing the difluoromethyl peak weights with a standard of a known concentrations of pure thenal.

Equal peak areas at different elution times do not represent the same number of molecules. However, after several attempts to use "pure" compounds to get a correspondence between the number of molecules and the peak areas at different elution times, the project was given up and everything referred to thenal. A conversion relationship was established as follows:

$$g(peak area) = \frac{g(thenal)}{g(solution)}$$

The weight of a compound (as thenal) was found from:

g(as thenal) = g (peak area) = g (soln) x g(soln) x g(soln) x (peak area) = g (soln) x (peak a

If the sum of the weights of the pertinent compounds (as thenal) did not equal the original weight of them, then some thenal was lost to secondary processes. It was found that thenal disappeared with longer times of reaction. Visual observation indicated that it was lost to an inky black polymer. Since the phenyl sulfur trifluoride is the more perishable of the reactants, the yields were calculated according to the equation:

g(thenal) std x 100% g(soln) std x g(peak area thenal)

Thenal gave a maximum yield of 22% after 3 hours at  $55^{\circ}$  and 5.5 hours at  $65^{\circ}$ . Smaller amounts were produced at lesser or greater times. An excess of thenal produced the largest yield of product. An unheated sample that was held in a refrigerator for several days gave no product and showed a loss of thenal to side reactions. Again, the progressively darkening reaction mixture qualitatively indicated a loss of reactants and/or products to polymerization.

Gas chromatography of small amounts of reaction mixtures showed that some difluoromethyl thiophene was formed. However, attempts to carry out the reaction in Pyrex glass resulted in complete failure to recover any product. It was, therefore, impossible to carry out the reaction sequence to make the bis-(difluoromethyl thenoyl) peroxide or the bis-(difluoromethyl furoyl) peroxide.

#### RESULTS AND DISCUSSION

A widely used method of preparing organic bis peroxides is the interaction of an organic solution of an acid chloride with an aqueous solution of sodium peroxide (6,7,8,11). Some difficulty was encountered in utilizing this procedure because of the uncertain purity of available sodium peroxide. The experimental procedure used in this study was that reported by Silbert and Swern (13) in their study of aliphatic bis peroxides.

The majority of the bis furoyl peroxides prepared in the course of this investigation were stable for short periods of time at room temperature. Crystalline bis-(5methyl-2-furoyl) peroxide was especially reactive and decomposed greatly in about a half day at room temperature. The mixed peroxides were stable and were usable after being set aside for a year at  $-20^{\circ}$ .

Tables I, II, and XIV and XV in the appendix give the melting points, analytical, and thermodynamic data for the peroxides prepared during this study. Figure I shows the relationship between the peroxides studied during this investigation, Plots of the individual peroxides can be found in the appendix.

The  $k/k_0$  ratio is a useful means of comparing the effects of a given substituent on the rate decomposition at

different temperatures of different series of compounds. The k value is the kinetic rate constant for the substituted compound and  $k_0$  is the kinetic rate constant for the unsubstituted parent compound. For any given series of compounds, the  $k/k_0$  ratio should be constant for small temperature ranges.

Decomposition rate data and  $k/k_0$  values at  $80^{\circ}$  for the compounds prepared in this study are to be found in Table I below. Comparative data for benzoyl and thenoyl peroxides can be found in the appendix.

Table I. Decomposition Rates of 2-Furoyl Peroxides at 80°

R	$K \ge 10^3 \text{ min}^{-1}$	k/ko
5-Methyl Bis-5-bromo Bis-5-chloro Furoyl-5-bromo Furoyl-5-chloro 2-Furoyl 3-Furoyl	69. 26.8 21.0 10.5 11.2 7.0 2.3	10. 3.8 3.0 1.5 1.6 1.0 0.3 (for com- parison)

A comparison of the  $k/k_0$  of the chloro and bromo substituted compounds show that the bis-(2-thenoyl) peroxides give effects similar to tertiary butyl perthenoates, i.e.,

Bis-(5-chloro-2-thenoyl)	0.71
Bis-(5-bromo-2-thenoy1)	0.70
t-Buty1-5-chloro-2-perthenoate	0.69
t-Buty1-5-bromo-2-perthenoate	0.67

and that bis benzoyl peroxides correspond to the bis-3thenoyl peroxides, i.e.,

Bis-(p-chloro-benzoyl)	0.86
Bis-(p-bromo-benzoyl)	0.77
Bis-(5-chloro-3-thenoyl)	0.87
Bis-(5-bromo-3-thenoy1)	0.79

On this basis, the Hammett function should apply to bis-3-thenoyl peroxides and apply approximately to the 2thenoyl derivatives. The halogen substitutions definitely cause a decrease in the rate of peroxide decomposition; the effect is in the same direction as that produced by the p-nitro group of tertiary butyl perbenzoate,  $k/k_0 = 0.332$ . Thus the deactivating effect must be due to electron withdrawal from the peroxide group. The further deactivating effect  $(k/k_0 = 0.71)$  produced by the second chloro group in bis-(2,5-dichloro-3-thenoyl) peroxide could be assumed to be due to an electron withdrawal caused by the additional chloro group. But the analogous bis-(2,4-dichloro-benzoyl) peroxide gives a large increase in the peroxide decomposition rate,  $k/k_0 = 10$ , and the bis-(5-nitro-2-thenoyl) peroxide yields a  $k/k_0$  value of 2.48. Depending upon the structures, the same kind of inductive effect can produce a more stable or a less stable peroxide oxygen-oxygen bond. This may be rationalized by assuming that if electron withdrawal becomes great enough to produce two opposing positive centers on the oxygens of the peroxide group it could cause the peroxide oxygen bond to rupture more easily.

It is interesting that the  $k/k_0$  values exhibited by chloro and bromo substitutions are very close to each other for any given ring system regardless of the ring system involved. This indicates that the effects produced by substitutions are a fundamental property of the substituted atom or group. The degree to which the effect is transmitted to the peroxide group depends on the ring system. The furan ring is much more effective in transmitting substituent effects than is the benzene ring or the thiophene ring. Indeed, the rates of decompositions produced by single halogen substituents on the furan ring are about 10 times as great as those produced by the same substituent on a benzene or thiophene ring.

For all the ring systems considered, alkyl substitution on a ring results in a greater rate of decomposition of the peroxide than is given by the unsubstituted compound,  $k/k_0 = 1.4-1.9$  for benzene and thiophene rings to  $k/k_0 = 10$ for the furan ring. A direct comparison of the k rates of methyl substituted rings shows that the furan ring is about 20 times as effective in affecting the decomposition rate as is the benzene ring or the thiophene ring. Since alkyl groups are classified as mild electron supplying groups, their effect upon the decomposition rate of the peroxide must be due to the production of opposing negative centers at the peroxide oxygen-oxygen bond.

Five mixed peroxides were prepared in this investigation, benzoyl-(2-furoyl), benzoyl-(2-thenoyl), benzoyl-(5-bromo-2-furoyl), 2-furoyl-(5-bromo-2-furoyl), 2-furoyl-(5-chloro-2-furoyl) and their decomposition rates were

determined over a range of at least 20°. Two of these, benzoyl-(2-thenoyl) and benzoyl-(2-furoyl) have previously been reported by Schuetz and Byrne (12) of these laboratories. The original log k vs 1/T plots made in this investigation for benzoyl-(2-thenoyl) peroxide did not correspond entirely to that plotted by Byrne. However, when more points were obtained at high temperatures the original results of this investigator and Byrne fitted acceptably as one plot.

When the rates of decomposition of these mixed peroxides are compared with the bis peroxides of the respective acyl groups, it is easily seen that the decomposition rates of the mixed peroxides have intermediate values. This is shown graphically in Figure 1 and summarized in Table XV.

The intermediate rate characteristic of unsymmetrical mixed peroxides allows for the preparation of a peroxide of almost any specific decomposition rate by mating appropriate acyl groups. A further use of mixed peroxides would be to estimate the rate of decomposition of a bis peroxide which in itself is unmanageable at ordinary temperatures. This might be an approach to the study of 5-nitro-2-furoyl peroxide.

3-Furoic acid is more stable than 2-furoic acid as is indicated by the preparation of 2-furoic acid from furan tetracarboxylic acid. The decomposition rate of 3-furoyl peroxide at 80<sup>°</sup> is about 1/3 of that of 2-furoyl peroxide.



The stability of the compound aids the stability of the peroxide. It would be of interest to determine the effect of alkyl and halogen substituents upon the decomposition rate of the 3-furoyl peroxides.

Halogens are electron withdrawing and alkyl groups are electro supplying. Since both kinds of groups accelerate the decomposition of furoyl peroxides when they are substituted on the furan ring it would be pertinent to determine the decomposition rate of an unsymmetrical 5-bromo-2-furoyl-(5-methyl-2-furoyl) peroxide in order to show whether the "opposing" forces would counteract or aid each other.

A further investigation would be to obtain kinetic and thermodynamic data for the t-butyl perfuroates to determine the effect of halogen substitutions on the decomposition rate. This work might shed some light on the intersection of the log k and 1/T plots of 2-furoyl-(5-bromo-2-furoyl) peroxide and 2-furoyl-(5-chloro-2-furoyl) peroxide and the convergence of the corresponding halogen bis peroxide plots.

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#### SUMMARY

Three previously unreported bis furoyl peroxides and three previously unreported unsymmetrical furoyl benzoyl mixed acyl peroxides were prepared. Decomposition rates and half lives over a range of temperatures were determined for eleven peroxides. From these data the energies and entropies of activation were determined.

As indicated by  $\frac{k}{k_0}$  values, the furan ring causes substituents to produce a more rapid decomposition of the peroxide grouping than is true of the thiophene or benzene rings. All decompositions of the peroxides were carried out in chloroform solution,  $0.2\underline{M}$  in styrene. The concentration of the peroxides at various stages of the kinetic determinations were found either by infrared measurements or by iodometric titrations.

A comparison of the rates of decomposition of the bis . peroxides with those of the mixed peroxides shows that the decomposition rates of the mixed peroxides are intermediate to those of the bis peroxides which may be assumed to have provided their acyl groups.

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APPENDIX

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Compound (peroxide)	Yield (percent)	M.P.	Equivalent Found	Weight Theory	Purity (percent)
Bis-(5-methyl-2-furoyl)	25	66-68	122-125	125	98
Bis-(5-chloro-2-furoy1)	70	111.5	149.5	145.5	97
Bis-(5-bromo-2-furoyl)	55	116-116.5	194	190	98
2-Furoy1-(5-chloro-2-furoy1)	66	91-92			
Benzoyl-(2-thenoyl)	67	93.5-94	120	124	97
Benzoyl-(2-furoyl)	51	61-61.5	121	116	96
Bis-(2-furoyl)	75	86-87	110.3	111	66
Benzoyl-(5-bromo-2-furoyl)	50	68-69	159	155.5	98
Bis-(3-furoyl)	57	74-75	109.5-111	111	66
2-Furoyl-(5-bromo-2-furoyl)	59	82.5-83.5	145	150	96.5

Table II. Peroxides Prepared

Table III. Analytical Data of Peroxides

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Compound (peroxide)	Formula	Analyt	ica]	l Data					
Bis-(5-methyl-2-furoyl)	Cl2H1006	Calc. Found	ບໍ່ບໍ່	57.6; 57.79;	н,	4.0 3.95			
Bis-(5-chloro-2-furoyl)	C10H406Cl2	Calc. Found	ບໍ່ບໍ່	41.20; 40.85;	н, Н,	1.29; 1.29;	с1, С1,	24.37 24.18	
Bis-(5-bromo-2-furoyl)	CloH406Brz	Calc. Found	ບໍ່ບໍ່	31.6; 31.54;	н,	1.05; 1.14;	В <b>г</b> , Вг,	42.1 41.90	
2-Furoyl-(5-chloro-2-furoyl)	C <sub>10</sub> H50 <sub>6</sub> Cl	Calc. Found	ບໍ່ບໍ່	46.81; 46.78;	н,	1.97; 1.93;	с1, С1,	13.82 13.94	
Benzoyl-(2-thenoyl)	C <sub>12</sub> H <sub>8</sub> O <sub>4</sub> S	Calc. Found	ບໍ່ບໍ່	58.15; 58.02;	н,	3.22; 3.12;	ີ ເດັ	12.90 12.90	
Benzoyl-(2-furoyl)	C <sub>12</sub> H <sub>8</sub> O5	Calc. Found	ບໍ່ບໍ່	62.2; 62.23;	н, Н,	3.45 3.49			
Benzoyl-(5-bromo-2-furoyl)	C <sub>12</sub> H704Br	<b>Calc.</b> Found	ບໍ່ບໍ່	46.3; 46.44;	н, н,	2.25; 2.29;	Br, Br,	25.7 25.5	
Bis-(3-furoy1)	C <sub>10</sub> H <sub>6</sub> O <sub>6</sub>	<b>Calc.</b> Found	ບໍ່ບໍ່	54.1 ; 53.69;	н,	2.70 2.57			
2-Furoyl-(5-bromo-2-furoyl)	C <sub>10</sub> H506Br	Calc. Found	ບໍ່ບໍ່	39.9; 40.19;	н,	1.66; 1.86;	Br, Br,	26.6 26.44	

Time		
(minutes	) Absorbance	Log A
Temperat	ure 31.0 <sup>a</sup>	
0 60 150 240 315	.302 .281 .275 .250 .244	-0.5200 -0.5513 -0.5607 -0.6021 -0.6126
Temperat	ure 37.0 <sup>b</sup>	
0 125 180 235	.302 .260 .250 .225	-0.5200 -0.5850 -0.6021 -0.6478
Temperat	ure 42.0	
0 90 120 150 180	.303 .245 .228 .226 .208	-0.5186 -0.6108 -0.6421 -0.6459 -0.6819
Temperat	ure 47.8 <sup>d</sup>	
0 10 20 40 60 60	.284 .276 .268 .245 .236 .225	-0.5467 -0.5591 -0.5719 -0.6108 -0.6271 -0.6478
<sup>a</sup> Slope:	2.9010 x $10^{-4}$ ; k: 6.6810 x $10^{-4}$	
<sup>b</sup> Slope:	5.1946 x $10^{-4}$ ; k: 1.1964 x $10^{-3}$	
<sup>C</sup> Slope: <sup>d</sup> Slope:	8.8745 x $10^{-4}$ ; k: 2.0438 x $10^{-3}$ 1.7188 x $10^{-3}$ ; k: 3.9583 x $10^{-3}$	

Table IV.	Infrared Information Leading to Kinetic Data of
	Bis-(5-methyl-2-furoyl) peroxide
	Solvent: CHCl <sub>3</sub> plus 0.2 <u>M</u> styrene

Time (minutes	)	M1 S <sub>2</sub> O <sub>3</sub> -	.2		Log ml
Temperat	ure 61.0 <sup>8</sup>	a			
15 75 150 225 300 390		20.9 18.8 14.8 12.8 10.3 8.0	95 90 95 99 97 96		1.3212 1.2742 1.1717 1.1103 1.0158 0.9063
Temperat	<u>ure 70.0<sup>1</sup></u>	C			
0 30 60 90 120 165		19.8 17.0 13.6 9.4 8.2 5.3	5 90 97 8 9 3		1.2978 1.2305 1.1358 0.9768 0.9186 0.7267
Temperat	ure 80.0 <sup>0</sup>	2			
2 15 30 45 60 75		21.6 17.0 13.1 9.1 6.9 5.5	8 94 .0 .5 1 8		1.3361 1.2315 1.1173 0.9814 0.8395 0.7466
Temperat	<u>ure 90.0<sup>6</sup></u>	1			
2 5 10 15 20		21.2 17.8 14.4 9.6 7.4	3 6 6 7 6		1.3270 1.2519 1.1602 0.9854 0.8727
<sup>a</sup> Slope:	1.1116 2	< 10 <sup>-3</sup> ; k:	2.5600	x 10 <sup>-3</sup>	
<sup>b</sup> Slope:	3.5226 2	( 10 <sup>-3</sup> ; k:	8.1123	х 10 <sup>-з</sup>	
<sup>C</sup> Slope: <sup>d</sup> Slope:	8.2719 x 2.5613 x	k 10 <sup>-3</sup> ; k: k 10 <sup>-2</sup> ; k:	1.9050 5.8987	x 10 <sup>-2</sup> x 10 <sup>-2</sup>	

Table V.	Titration Information Leading to Kinetic Data of	=
	Bis-(5-chloro-2-furoyl) peroxide	
	Solvent: CHCl <sub>3</sub> plus 0.2 <u>M</u> styrene	

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Time		<b>T</b> an m1
(minutes	$S_2 O_3 =$	LOG MI
Temperat	<u>ure 61.0</u> <sup>a</sup>	
15	13.31	1.1242
150	9.40	0.9731
300	6.75	0.8293
390	4.67	0.6693
Temperat	<u>ure 70.0</u> <sup>b</sup>	
0	8.08	0,9074
60	4.29	0.6325
90	3.00	0.4771
165	1.02	0.0086
	<b>2</b>	
Temperat	<u>ure 80.0</u>	
2	16.67	1.2219
15	12.62	1.1011
30 45	8.4 <i>1</i> 5.78	0.9279
40 60	3.75	0.5740
75	2.42	0.3838
Temperat	ure 90.0 <sup>d</sup>	
2	13.53	1.1313
4	12.03	1.0803
6 9	10.15	0.8859
12	6.50	0.8129
	$1 1685 \times 10^{-3}$ . Let 2 6850 $\times 10^{-3}$	
b <sub>slope</sub> .	$5.4728 \times 10^{-3}$ . $1.2600 \times 10^{-3}$	-2
Celoner	$1 1154 = 10^{-2}$ . L. $2 5677 = 10$	-2
d <sub>class</sub>	7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	-2
stope:	$3.3240 \times 10^{}$ ; K: $7.6552 \times 10^{}$	

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Table VI.	Titration Information Leading to Kinetic Data of	£
	Bis-(5-bromo-2-furoyl) peroxide	
	Solvent: CHCl <sub>3</sub> plus 0.2 <u>M</u> styrene	

Time (minutes	3)	M1 S <sub>2</sub> O <sub>3</sub> -2	Log ml
Temperat	ure 61.0 <sup>a</sup>		
15 15 150 225 390		16.32 16.70 14.77 13.30 10.64	1.2127 1.2227 1.1694 1.1239 1.0269
Temperat	ure 70.0 <sup>D</sup>		
0 30 60 90 120 165		18.22 16.53 14.90 13.39 12.00 9.72	1.2606 1.2183 1.1732 1.1268 1.0792 0.9877
Temperat	ure 80.0 <sup>C</sup>		
2 15 30 45 60 75		17.00 14.96 12.81 10.77 8.79 7.62	1.2305 1.1749 1.1076 1.0322 0.9440 0.8820
Temperat	ure 90.0 <sup>d</sup>		
2 5 20 30 40		15.92 13.74 8.13 6.34 4.37	1.2019 1.1380 0.9101 0.8021 0.6405
<sup>a</sup> Slope:	5.0197 x 10 <sup>-4</sup>	; k; 1.1560 :	к 10 <sup>-3</sup>
<sup>b</sup> Slope:	1.6342 x 10 <sup>-2</sup>	; k: 3.7632	к 10 <sup>-3</sup>
<sup>C</sup> Slope:	4.8781 x $10^{-3}$	; k: 1.1234 :	x 10 <sup>-2</sup>
<sup>a</sup> Slope:	$1.4382 \times 10^{-2}$	; k: 3.3121 :	x 10 <sup>-2</sup>

Table VII.	Titration Information Leading to Kinetic Data of
	2-Furoyl-(5-chloro-2-furoyl) peroxide
	Solvent: CHCl <sub>3</sub> plus 0.2 <u>M</u> styrene

Time (minutes)	M1 S <sub>2</sub> O <sub>3</sub> -2	Log ml
Temperature 70.0	a	
180 240 305 390 490 680	8.94 8.46 8.15 7.40 6.30 5.28	0.9513 0.9274 0.9112 0.8692 0.7993 0.7226
Temperature 75.0	b	
75 165 210 240 360	8.75 7.20 6.87 6.52 5.52	0.9420 0.8573 0.8370 0.8142 0.7419
Temperature 80.0	C	
60 95 130 165 375	7.5 6.8 6.1 5.8 3.2	0.8751 0.8325 0.7853 0.7634 0.5051
Temperature 80.0	đ	
2 60 120 240 360 480	28.80 23.58 19.64 13.32 9.15 6.63	1.4594 1.3725 1.2951 1.1245 0.9614 0.8215
Temperature 90.0	e	
2 30 60 90 120 150	29.18 22.12 16.36 12.87 9.22 7.07	1.4651 1.3448 1.2138 1.1096 0.9647 0.8494

Table VIII. Titration Information Leading to Kinetic Data of Benzoyl-(2-thenoyl) peroxide Solvent: CHCl<sub>3</sub> plus 0.2 <u>M</u> styrene

continued

Time (minutes	:)	S	M1 5203-	2			 Log ml	
Temperat	ure 100.0	) <sup>f</sup>					 	
2 10 20 30 40 50			27.10 20.92 16.03 11.60 8.54 6.34				1.4330 1.3206 1.2049 1.0645 0.9315 0.8021	
<sup>a</sup> Slope: <sup>b</sup> Slope: <sup>c</sup> Slope: <sup>d</sup> Slope: <sup>e</sup> Slope: fslope:	4.7393 x 6.8803 x 1.1497 x 1.3422 x 4.1560 x 1.3123 x	$10^{-4};$ $10^{-4};$ $10^{-3};$ $10^{-3};$ $10^{-3};$ $10^{-2};$	k: k: k: k: k: k:	1.0915 1.5845 2.6472 3.0911 9.5722 3.0215	x x x x x x x x	10 <sup>-3</sup> 10 <sup>-3</sup> 10 <sup>-3</sup> 10 <sup>-3</sup> 10 <sup>-2</sup>		

Table VIII - continued

Time (minutes)		M1 S <sub>2</sub> O <sub>3</sub> -2		Log ml
Temperatu	are 70.0 <sup>a</sup>			
0 120 180 240 305 390 490 680		11.27 9.55 9.20 8.52 8.05 7.05 5.70 4.70		1.0519 0.9800 0.9638 0.9304 0.9058 0.8482 0.7559 0.6721
Temperatu	<u>ire 75.0</u> <sup>b</sup>			
78 165 200 304		9.2 6.4 6.5 4.8		0.9638 0.8062 0.8129 0.6812
Temperatu	<u>re 80.0</u> <sup>C</sup>			
20 50 92 170 240		15.19 13.62 11.37 7.88 6.61		1.1816 1.1342 1.0576 0.8965 0.8202
Temperatu	are 80.0 <sup>d</sup>			
3 60 120 180 240 300		23.86 18.75 14.81 12.21 8.47 6.86		1.3777 1.2730 1.1706 1.0867 0.9279 0.8363
Temperatu	<u>re 90.0</u> <sup>e</sup>			
2 20 40 80 90 100		19.65 14.77 11.30 5.91 4.95 4.21		1.2934 1.1694 1.0531 0.7716 0.6946 0.6243
à b Slope: c Slope: d Slope: e Slope:	5.7145 x 1.2089 x 1.7074 x 1.8353 x 6.8179 x	$10^{-4}$ ; k: 1.3 $10^{-3}$ ; k: 2.7 $10^{-3}$ ; k: 3.9 $10^{-3}$ ; k: 4.2 $10^{-3}$ ; k: 1.5	$160 \times 10^{-3}$ $340 \times 10^{-3}$ $321 \times 10^{-3}$ $259 \times 10^{-3}$ $701 \times 10^{-2}$	

Table IX.	Titration	Information	Leading	to 1	Kinetic	Data	of	
		Benzoy1-2-	-furoyl peror	kide –				
		Solvent:	CHCl <sub>3</sub> plus (	0.2 <u>M</u> sty	yren	е		

		المراقع المراجعين الترجيع المراجع المراجع المراجع والمراجع المراجع المراجع والمراجع المراجع المراجع المراجع ال مستريب من المراجع المراجع المراجع في من المراجع المراجع المراجع المراجع المراجع المراجع المراجع المراجع المراجع
Time (minutes	$S_{2}O_{3}^{-2}$	Log ml
Temperat	ure 70.0 <sup>a</sup>	
120 180 390	11.23 10.05 6.91	1.0492 1.0043 0.8395
Temperat	<u>ure 75.0</u> <sup>b</sup>	
75 165 240 360	12.90 7.34 6.00 4.47	1.1106 0.8657 0.7782 0.6503
Temperat	ure 80.0 <sup>C</sup>	
2 60 120 180 240 240 300 360 420 420 420 480 Temperat	19.78 9.95 8.27 5.00 3.45 3.20 1.95 1.84 0.87 0.62 0.65	1.2962 0.9978 0.9175 0.6990 0.5391 0.5052 0.2900 0.2648 -0.0605 -0.2076 -0.18709
1 15 30 45 60 75	44.22 32.80 22.75 15.85 10.71 7.74	1.6450 1.5159 1.3570 1.2000 1.0298 0.8887
Temperat	<u>ure 100.0</u>	4 0747
1.4 5 10 20	43.08 34.40 21.70 12.36	1.6343 1.5366 1.3365 1.0920
aslope: bslope: cslope: dslope: ëslope: slope:	7.7944 x $10^{-4}$ ; k: 1.7950 x 10 1.5577 x $10^{-3}$ ; k: 3.5874 x 10 3.1410 x $10^{-3}$ ; k: 7.2336 x 10 1.0381 x $10^{-2}$ ; k: 2.3907 x 10 3.6860 x $10^{-2}$ ; k: 6.7993 x 10	-3 -3 -3 -2 -2

Table X.	Titration Information Leading to Kinetic Data of Bis-(2-furoyl) peroxide			
	Solvent: CHCl <sub>3</sub> plus 0.2 <u>M</u> styrene			
Time (minutes	;)	M1 S <sub>2</sub> O <sub>3</sub>	-2	Log ml
---	--	--	--	--
Temperat	ure 70.0 <sup>a</sup>			
0 120 180 305 390 490 625 680		5.7 4.44 3.9 3.08 2.8 1.84 1.73 1.62	7 1- 7 3 7 1- 5 2	0.7612 0.6474 0.5988 0.4886 0.4579 0.2648 0.2380 0.2095
Temperat	ure 75.0 <sup>D</sup>			
75 165 210 240		4.70 3.30 2.88 2.60	) ) }	0.6721 0.5185 0.4594 0.4150
Temperat	ure 80.0 <sup>C</sup>			
60 95 130 165 195	_	3.8 3.1 2.65 2.1 1.9	5	0.5798 0.4914 0.4232 0.3222 0.2788
Temperat	<u>ure 80.0</u> <sup>d</sup>			
2 30 90 150 210 295		17.20 14.53 10.72 7.98 5.23 3.01	) 5 2 3 7	1.2355 1.1623 1.0302 0.9021 0.7218 0.4786
Temperat	<u>ure 90.0</u> <sup>e</sup>			
2 20 40 80		13.55 10.35 6.54 2.32		1.1319 1.0166 0.8156 0.3655
a Slope: cSlope: dSlope: eSlope: eSlope:	7.9593 x 1.5574 x 2.2723 x 2.5490 x 1.0033 x	$10^{-4}$ ; k: $10^{-3}$ ; k: $10^{-3}$ ; k: $10^{-3}$ ; k: $10^{-2}$ ; k:	1.8757 3.5867 5.2330 5.7367 2.3106	

Table XI. Titration Information Leading to Kinetic Data of Benzoyl-(5-bromo-2-furoyl) peroxide Solvent: CHCl<sub>3</sub> plus 0.2 <u>M</u> styrene

Time (minutes	5)	Absorbance	Log A
Temperat	cure 61.0 <sup>a</sup>		
0 203 501 1180 1935		.500 .470 .440 .390 .358	-0.3010 -0.3279 -0.3565 -0.4089 -0.4461
Temperat	ure 65.2 <sup>b</sup>		
0 180 300 605		.500 .463 .458 .410	-0.3010 -0.3344 -0.3391 -0.3872
Temperat	ure 71.2 <sup>C</sup>		
0 90 150 200 420		.500 .470 .460 .440 .388	-0.3010 -0.3279 -0.3372 -0.3565 -0.4112
a b Slope: c Slope:	7.3720 x 10 <sup>-</sup> 1.3813 x 10 <sup>-</sup> 2.6101 x 10 <sup>-</sup>	<sup>5</sup> ; k: 1.6978 x 10 <sup>4</sup> ; k: 3.1812 x 10 <sup>4</sup> ; k: 6.0110 x 10	- 4 - 4 - 4

Table XII-A.	Infrared I	Information	Leading	to	Kinetic	Data	of
	Bis-(3-fur	oyl) peroxi	lde				
	Solvent:	CHCl <sub>3</sub> plus	0.2 <u>M</u> st	yre	ene		

Time (minutes)	M1 S <sub>2</sub> O <sub>3</sub> -2	Log_ml
Temperature 80.	.0 <sup>a</sup>	
4 120 160 450 480	18.68 14.04 10.18 6.45 6.31	1.2614 1.1474 1.0078 0.8096 0.8000
Temperature 90.	.0 <sup>b</sup>	
2 40 80 120 180 240	15.22 10.95 8.03 5.17 3.47 1.46	1.1824 1.0394 0.9047 0.7135 0.5403 0.1644

Table XII-B.	Titration	Information	Leading	to Kinetic	Data	of
	Bi <b>s-(</b> 3-fu:	royl) peroxid	de			
	Solvent:	CHCl <sub>3</sub> plus	0.2 <u>M</u> sty	rene		

<sup>a</sup>slope:  $9.4332 \times 10^{-4}$ ; k:  $2.1725 \times 10^{-3}$ 

<sup>b</sup>Slope: 4.1355 x 10<sup>-3</sup>; k: 9.5206 x 10<sup>-3</sup>

Time (minutes	) $S_2 O_3^{-2}$	Log ml
Temperat	<u>ure 70.0</u> <sup>a</sup>	
0 30 60 90 120 165	11.34 11.11 10.41 8.85 9.20 7.46	1.0546 1.0457 1.0175 0.9469 0.9638 0.8727
Temperat	<u>ure 75.0</u> <sup>b</sup>	
60 115 175 <b>225</b>	5.6 4.3 3.2 2.5	0.7482 0.6335 0.5051 0.3979
Temperat	ure 80.0 <sup>C</sup>	
20 50 90 170	6.4 4.6 3.4 1.6	0.8062 0.6628 0.5315 0.2041
Temperat	<u>ure 80.0</u> <sup>d</sup>	
15 30 45 60 75	11.63 9.79 8.45 7.52 5.94	1.0656 0.9908 0.9269 0.8762 0.7738
Temperat	ure 90.0 <sup>e</sup>	
2 5 10 20 30	5.68 4.02 3.10 1.96 1.41	0.7544 0.6042 0.4914 0.2923 0.1492
a bSlope: cSlope: dSlope: eSlope: eSlope:	1.1024 x $10^{-3}$ ; k: 2.5388 x $10^{-3}$ 2.1243 x $10^{-3}$ ; k: 4.8921 x $10^{-3}$ 3.9510 x $10^{-3}$ ; k: 9.0992 x $10^{-3}$ 4.6547 x $10^{-3}$ ; k: 1.0720 x $10^{-2}$ 2.0594 x $10^{-2}$ ; k: 4.7428 x $10^{-2}$	

Table XIII. Titration Information Leading to Kinetic Data of 2-Furoyl-(5-bromo-2-furoyl) peroxide Solvent: CHCl<sub>3</sub> plus 0.2 <u>M</u> styrene

Compound (peroxide)	k (min- x 10 <sup>3</sup>	ı)	-Log k	( <sup>T</sup> K)	1/т х 10 <sup>3</sup>	t <sup>1</sup>
Bis-(5-methyl-2- furoyl)	0.6681 1.196 2.044 3.958		3.1752 2.9222 2.6896 2.4025	304.0 310.0 315.0 320.8	3.289 3.225 3.174 3.117	1037.0 579.3 339.1 175.1
Bis-(5-chloro-2- furoyl)	2.560 8.112 19.05		2.5918 2.0909 1.7201	334.0 343.0 353.0	kcal. 2.994 2.915 2.833	270.7 85.4 36.4
	58.99 Energy	of	1.2292 activation	363.0 n: 24.0	2.754 kcal.	11.8 mole <sup>-1</sup>
Bis-(5-bromo-2- furoy1)	2.685 12.60 25.58 76.55		2.5711 1.8995 1.5755 1.1161	334.0 343.0 353.0 363.0	2.994 2.915 2.833 2.754	258.1 54.9 26.1 9.05
	Energy	of	activation	n: 26.3	kcal.	mole <sup>-1</sup>
2-Furoyl-(5-chloro- 2-furoyl)	1.156 3.763 11.23 33.12 Energy	of	2.9370 2.4244 1.9495 1.4799 activation	334.0 343.0 353.0 363.0 n: 27.6	2.994 2.915 2.833 2.754 kcal.	599.5 184.1 61.7 20.9 mole <sup>-1</sup>
Benzoyl-2-thenoyl	1.092 1.585 2.647 3.091 9.572 30.22 Energy	of	2.9620 2.8001 2.5701 2.5098 2.0190 1.5197 activation	343.0 348.0 353.0 353.0 363.0 373.0 a: 28.9	2.915 2.874 2.833 2.833 2.754 2.681 kcal.	635.9 437.4 257.5 224.2 72.4 22.93 mole <sup>-1</sup>
Benzoyl-(2- furoyl)	1.316 2.784 3.932 4.226 15.70		2.8807 2.5553 2.4054 2.37408 1.8041	343.0 348.0 353.0 353.0 363.0	2.915 2.873 2.833 2.833 3.754	438.0 248.9 176.2 164.0 44.1
	Energy	of	activation	n: 29.8	3 kcal	. mole <sup>-1</sup>

Table XIV. Summary of Kinetic Data

continued

Compound (peroxide	k (min <sup>-</sup> x 10 <sup>3</sup>	ı)	, -Log k (	с К)	1/T x 10 <sup>3</sup>	t <sup>2</sup>
Bis-(2-furoyl)	1.795 3.587 7.234 23.91 67.99 Energy	of	2.7459 2.4452 2.1406 1.6215 1.1675 activations	343.0 348.0 353.0 363.0 373.0 : 30.6	2.915 2.874 2.833 2.754 2.681 kcal.	386.1 193.2 76.1 29.0 10.2 mole <sup>-1</sup>
Benzoyl-(5-bromo- 2-furoyl)	1.876 3.587 5.233 5.737 23.11 Energy	of	2.7268 2.4453 2.2813 2.2313 1.6363 activation	343.0 348.0 353.0 353.0 363.0 363.0	2.915 2.874 2.833 2.833 2.754 kcal.	369.5 193.2 132.4 118.1 30.0 mole <sup>-1</sup>
Bis-(3-furoyl)	0.1698 0.3181 0.6011 2.173 9.521 Energy	of	3.7701 3.4974 3.2211 2.6630 2.0213 activation	534.0 538.2 544.2 553.0 563.0 : 31.9	2.994 2.956 2.905 2.833 2.754 kcal.	4081.0 2178.0 1153.0 319.0 72.8 mole <sup>-1</sup>
2-Furoyl-(5-bromo- 2-furoyl)	2.539 4.892 9.099 10.72 47.43 Energy	of	2.5954 2.3105 2.0410 1.9698 1.3240 activation	343.0 348.0 353.0 353.0 363.0 363.0	2.915 2.874 2.833 2.833 2.754 kcal.	274.0 141.7 76.2 64.6 14.6 mole <sup>-1</sup>

Table XIV - continued

Compound (peroxide) k	act cal. mole <sup>-1</sup>	Log s	Temp. (K)	Entropy of activation cal. deg. <sup>-1</sup> mole <sup>-1</sup>
Bis-(5-methy1-2-furoy1)	20.6	11.5464	353	-7.826
Bis-(5-chloro-2-furoyl)	24.0	13.1522	353	-0.4722
Bis-(5-bromo-2-furoy1)	26.3	14.8975	353	7.511
2-Furoy1-(5-chloro- 2-furoy1)	26.6	15.1483	353	8.670
Benzoyl-(2-thenoyl)	28.9	15.3050	353	9.388
Benzoyl-(2-furoyl)	29.8	16.0628	353	12.86
Bis-(2-furoy1)	30.6	16.8827	353	16.62
Benzoyl-(5-bromo-2-furoyl)	30.5	16.6592	353	15.59
Bis-(3-furoyl)	31.9	17.1024	353	17.62
2-Furoyl-(5-bromo-2-furoyl	.) 33.0	18.4530	353	23.81

Table XV. Calculation of Entropies of Activation

Substituent (D)	$1 - 10^3 - 1$	1- /1-
Substituent (R)		к/к <sub>о</sub>
Benzoyl peroxides at	<u>= 80</u> ° (6)	
p methyl p hydrogen p chloro p bromo 2.4 dichloro	3.68 2.52 2.17 1.94	1.46 1.00 0.86 0.77 10.00 (25)
Tertiary butyl perbe	enzoate at 110 <sup>0</sup> (7)	
p methyl p hydrogen p chloro p nitro	0.115 0.082 0.0665 0.0272	1.4 1.0 0.81 0.33
Tertiary butyl perth	nencates at 99.3 <sup>0</sup> (7)	
5 ethyl 5 methyl 5 hydrogen 5 chloro 5 bromo	0.325 0.281 0.201 0.138 0.135	1.6 1.4 1.0 0.69 0.67
Bis-2-thenoyl peroxi	<u>ides at 79.6</u> ° (8)	
5 nitro 2,5 dimethyl 5 hydrogen 5 bromo 5 chloro 2,5 dichloro	5.85 3.79 2.36 2.03 1.86 1.68	2.48 1.60 1.00 0.87 0.79 0.71
Bis-2-thenoyl peroxi	<u>des at 75</u> 0 (6)	
5 methyl 5 methyl-2-thenoy (2-thenoyl) 5 hydrogen bis-3-thenoyl 5 chloro 5 bromo 4 bromo	2.54 1.79 1.33 1.29 0.95 0.92 0.69	1.9 1.35 1.00 0.97 (for compariso 0.71 0.70 0.52

Table XVI. Decomposition Rates of Peroxides for Comparison with Table I.



Figure 2. Activation energy of bis-(5-methyl-2-furoyl) peroxide.



Activation energy of bis-(5-chloro-2-furoyl) peroxide.







Figure 5. Activation energy of 2-furoyl-(5-chloro-2-furoyl) peroxide.



Figure 6. Activation energy of benzoyl-(2-thenoyl) peroxide.



Figure 7. Activation energy of benzoyl-(2-furoyl) peroxide.



Activation energy of bis-(2-furoyl) peroxide. Figure 8.



Figure 9. Activation energy of benzoyl-(5-bromo-2-furoyl) peroxide.



Figure 10. Activation energy of bis-(3-furoyl) peroxide.



Figure 11. Activation energy of furoyl-(5-bromo-2-furoyl) peroxide.

