formate and unbound water in the liquid or gaseous state

$$2HCOOHg \cdot H_2O + H_2O = HCOOH + CO_2 + 2Hg + 3H_2O$$

A trace of water on the crystal or in the vapor is sufficient to start the reaction, and the extra water released makes the decomposition of additional molecules of formate possible.

In order to interpret the rate data on the pure solid, we set up the following tentative mechanism: The reaction occurs heterogeneously between the crystal and water either in the vapor or the liquid phase. The amount of reaction which has occurred during the induction period is so small that we can consider the activity of the formate unchanged, and the rate controlled entirely by the changing partial pressure of water. After the induction period, the partial pressure of water is constant and equal to the saturation value, and the rate will be controlled only by the activity of the formate.

A mathematical analysis based on this mechanism leads to the equations

$$\log \frac{n}{n_\infty} = \frac{kp^0 n_\infty t}{2.303\ n_\tau} - \frac{kp^0 n_\infty}{2.303\ n_\tau} + \log \frac{n_\tau}{n_\infty} \quad t \leq \tau \quad (1)$$

and

$$\log \frac{n_\infty - n}{n_\infty} = -\frac{kp^0 t}{2.303} + \frac{kp^0 \tau}{2.303} + \log \frac{n_\infty - n_\tau}{n_\infty} \quad t \geq \tau \quad (2)$$

where

n = moles of CO_2 produced at any time, t

n_τ = moles of CO_2 produced at time τ, the end of the induction period

n_∞ = moles of CO_2 produced at end of reaction

p^0 = saturation vapor pressure of water

Equation 2 expresses mathematically the required first order rate law, where the apparent rate constant is seen to be equal to kp^0. These apparent rate constants vary much more sharply with temperature than required by the Arrhenius equation. Vapor pressures for the three temperatures studied can, however, be estimated from the data of Takagi,[3] and values of k can thus be determined. Sufficient data are not available for an exact treatment, but the composition of the vapor is close enough to that of the constant boiling mixture so that we may approximate the actual vapor pressure by the latter. The results, given in Table I, show that in all three cases the saturation pressure is below the partial pressure indicated by the stoichiometry, and condensation will therefore occur. Values of k thus derived obey the Arrhenius equation. This in itself constitutes some verification of our proposed mechanism. The activation energy is 16.6 ± 1 kcal.

TABLE I

SUMMARY OF RATE DATA

t, °C.	p^0, atm.	k (atm.$^{-1}$ sec.$^{-1}$) × 10^3
75.3	0.30	0.76
80.0	.36	1.00
94.4	.62	2.54

Other points to be noted on examination of the data in the light of Equations 1 and 2 are the following: (1) During the induction period, experimental values of log n/n_∞ are a linear function of t, as required by Equation 1. (2) Values of τ and n_τ/n_∞ derived from slopes and intercepts of both equations are self consistent at all temperatures. (3) Derived values of τ are strictly proportional to the product kp^0. (4) Within the limits of error, n_τ/n_∞ is the same for all temperatures. Its value is 0.11. In other words, the induction period is over when 11% decomposition has occurred, regardless of temperature. (5) The fact that consistent values of k (or more accurately kp^0) are obtained through both Equations 1 and 2 is evidence that precisely the same reaction is occurring before and after the induction period, as required by the proposed mechanism.

Thus the proposed mechanism seems amply verified not only by the observed effect of water on the reaction, but also by the excellent fit of the data to equations derived on the basis of the mechanism, the consistency of constants obtained from the equations, and the agreement of the actual rather than the apparent rate constants with the Arrhenius equation. On the other hand, we have not attempted to consider in detail the disintegrating crystal lattice during the induction period, and the mechanism cannot therefore be established at this time as unique.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON 6, WIS.
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(3) Takagi, *Bull. Chem. Soc. Japan*, **14**, 508 (1939).

Bis-(substituted phenoxy)-methanes[1]

BY SIMON MIRON[2] AND ALEXANDER LOWY[3]

Varying yields, generally below 45%, have been reported in the literature for the Williamson-type synthesis between alkali-metal phenolates and methylene halides to produce bis-(substituted phenoxy)-methanes. The following procedure was employed to give consistently good yields of these compounds:

A methanolic solution of sodium hydroxide of normality approximately 1 was used to convert the phenols to their sodium salts. This solution was standardized prior to each synthesis by titration against standard acid. A weighed quantity of the pure phenolic compound was neutralized with the theoretical quantity of alkali in a round-bottom reaction flask. After removal of the methanol by distillation under reduced pressure, the equivalent amount, or slightly less, of pure methylene iodide was added to the flask, together with enough 3-methylbutanol to keep the reactants in solution at reflux temperature, and the mixture was refluxed for two to twelve hours. Following the reflux period, solvent was removed under reduced pressure and the crude residue was partially purified by repeated treatment with boiling aqueous potassium hydroxide solution (0.5–1.0%), until the alkaline extracts gave no phenolic precipitate upon acidification. The product was then washed free of alkali, dried and crystallized from a suitable solvent.

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(1) Taken from Part I of the dissertation presented by Simon Miron in August, 1941, in partial fulfillment of the requirements for the Ph.D. degree.

(2) Pan American Refining Corporation, Texas City, Texas.

(3) Deceased December 25, 1941.

TABLE I

PREPARATION, PROPERTIES AND ANALYSIS OF BIS-(SUBSTITUTED PHENOXY)-METHANES[a]

Substituent and position	Reflux period, hours	Crystallizing solvent	Yield, %	Melting point, °C. (cor.)[b]	Carbon, %		Hydrogen, %		Halogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
p-Phenyl	2	Acetone	63	180.2–180.9	85.20	85.28	5.72	5.81		
o-Phenyl	3	70% ethanol	54	104.0–104.8	85.20	85.20	5.72	5.82		
p-*t*-Amyl	8	[d]	64[d]	41.5–41.9[e]	81.13	81.17	9.47	9.36		
o-Cyclohexyl	5	85% ethanol	53	95.8–96.6	82.39	82.46	8.85	9.00		
p-Benzyl	6	95% ethanol	59	74.8–75.4	85.21	85.40	6.36	6.53		
p-Chloro[f,h,i]	6	Pet. ether	62	69.7–70.2[f,i]					26.34[j]	26.45[j]
o-Chloro[g,h]	6	Pet. ether	57	87.8–88.6					26.34[j]	26.37[j]
2,4-Dichloro[h]	4$^1/_2$	80% ethanol	74	100.4–100.8	46.19	46.12	2.38	2.41		
p-Bromo[h,i]	3	80% ethanol	62	74.0–74.5[i]	43.59	43.58	2.82	2.89	44.63[k]	45.09[k]
p-Formyl	12	50% ethanol	60	84–85[l]	70.35	70.26	4.72	4.89		

[a] All compounds are new except those indicated by footnotes, *f*, *g*, *h* and *i*. [b] All melting points were run on samples which were recrystallized several times, generally from different solvents. [c] Average of two values. [d] This low melting product was distilled at 1 mm. pressure, and the yield was based on a fraction boiling within a 3° range. [e] Boiling point 185–186° at 1 mm. pressure. [f] Patented as an insect toxicant by the Dow Chemical Co., Brit. Appl. 16,328, filed June 20, 1947, conv. date May 1, 1942. Melting point listed as 67–69°. [g] The Dow patent cited in footnote *f* states that bis-(2-chlorophenoxy)-methane may be used as an insect toxicant, but no properties of the compound are presented. [h] E. E. Kenaga, *J. Econ. Entomol.*, **42**, 996 (1949) mentions that bis-(*p*-chlorophenoxy)-methane, bis-(*o*-chlorophenoxy)-methane, bis-(2,4-dichlorophenoxy)-methane and bis-(*p*-bromophenoxy)-methane were tested for acaricidal activity, but no properties of the compounds are presented. [i] R. L. Metcalf, *J. Econ. Entomol.*, **41**, No. 6, 875 (1948) lists the melting point of bis-(*p*-chlorophenoxy)-methane as 70–72°, and that of bis-(*p*-bromophenoxy)-methane as 74–75°. [j] Chlorine. [k] Bromine. [l] On rapid heating the m.p. is 84–85°. On slow heating the compound softens at about 82° and shrinks to a turbid, jelly-like mass which eventually melts to a clear, isotropic liquid, then solidifies at a higher temperature, and finally remelts (dec.) above 240°. Complete resolidification results after keeping the compound at 115° for about an hour; b.p. (1 mm.), 218–219°, b.p. (2 mm.) 233–234°.

Table I summarizes the data on preparation, analysis and melting point of ten bis-(substituted phenoxy)-methanes prepared by the above procedure, yields being based upon the once-crystallized product. These compounds are new with the exception of the four which are indicated in the table, and which are included because their preparation and properties are incompletely described in the literature.[4]

The compounds listed in Table I are insoluble in water, but soluble in acetone, 95% ethanol, benzene, petroleum ether and glacial acetic acid. In the presence of hot, concentrated sulfuric acid they give rise to deep red, green, orange or brown solutions.

Bis-(*p*-phenylphenoxy)-methane is quite stable to the action of alkali, either in aqueous or ethanolic solution, no detectable change being produced by two hours of refluxing with a 50% solution of potassium hydroxide in 95% ethanol. It is also inert to potassium permanganate in neutral medium; a sample shows no change after 100 hours of refluxing in the presence of 2% aqueous potassium permanganate. In acid solution, on the other hand, the compound appears to be completely oxidized by the permanganate.

Bis-(*p*-formylphenoxy)-methane exhibits most of the characteristic properties of aldehydes. It immediately reddens Schiff reagent in aldehyde-free ethanol solution, produces a good silver mirror with Tollens reagent, forms a crystalline compound with sodium bisulfite, and reduces an acetone solution of potassium permanganate in the cold. Fehling solution, on the other hand, is only slightly reduced after prolonged heating.

The melting behavior of bis-(*p*-formylphenoxy)-methane, described in footnote (1) of Table I, is unusual. A somewhat similar phenomenon has been observed by Neish[5] in an analogous compound, 4,4′-tetramethylene dioxydibenzaldehyde, which was reported to melt with turbidity at 110° and to clear up at 130–140°. Neish suggested that this behavior was caused by partial oxidation at the melting point.

The cleavage of the methylenedioxy group for characterization purposes was accomplished for the ten compounds of Table I by a modification of the procedure of Clowes and Tollens,[6] using phloroglucinol as a formaldehyde binder. A mixture of 0.0019 mole of the compound, 0.0019 mole (0.30 g.) of phloroglucinol, 8.0 ml. of 12 *N* HCl, and 30–40 ml. of glacial acetic acid was refluxed for 12 hours. A red precipitate of the formaldehyde phloroglucide generally formed within a few minutes. Distillation of the mixture under reduced pressure left a solid residue consisting chiefly of the phloroglucide and liberated phenolic compound. The phenol was separated from the cleavage residue by steam distillation or solvent extraction, and was identified by its properties and by the formation of a suitable derivative. Yields of recovered phenols varied from 4 to 40%.

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[4] All ten compounds were new at the time this work was completed [*cf. University of Pittsburgh Bulletin*, **38**, No. 2, 294–300 (1942)] but priority for the synthesis of four of them was forfeited because of delay in submitting the work for publication.

(5) W. J. P. Neish, *Rec. trav. chim.*, **66**, 433 (1947).

(6) G. H. A. Clowes and B. Tollens, *Ber.*, **32**, 2841 (1899).

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF PITTSBURGH
PITTSBURGH, PENNSYLVANIA

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Synthesis in the Pyridazine Series. I. Pyridazine and 3,6-Dichloropyridazine

BY R. H. MIZZONI AND PAUL E. SPOERRI

Existing methods for the preparation of pyridazine are in the main cumbersome and characterized by poor yields. The first recorded syn-