TABLE II

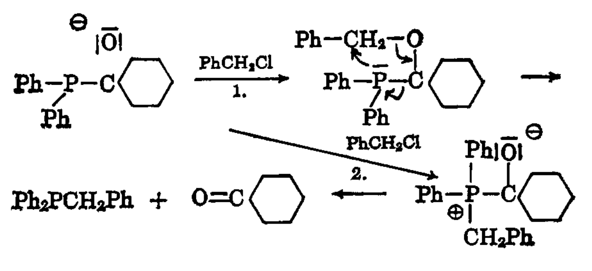
Multiplet centers, p.p.m.		Assignment, *cf.* 1	Relative area
0.85	Multiplet	a	3
1.4	Multiplet	b	4
3.2			
3.32		c	2
3.42			
3.55			
7.45	Multiplet	d	10
7.85	Multiplet		
8.64		e	1

form and an internal standard of tetramethylsilane were employed. The spectrum for the butyl derivative VI with peak assignments and relative integrated areas are summarized in Table II. The quartet in the region centering at 3.37 p.p.m. is indicative of the NH and CH_2 groups adjacent to this methylene.

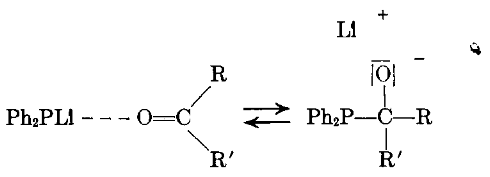
Essentially similar results were obtained with the ethyl derivative VIII. Spectra of the phenyl V and *p*-bromophenyl VII compounds showed signals only in the area assigned to phenyl protons. In the latter compounds the NH proton resonance appeared further downfield than in the aliphatic derivates, falling at 10.3 p.p.m. and 10.9 p.p.m., respectively. This is in agreement with the decrease in shielding expected on replacement of aliphatic by aromatic substituents and substitution in the ring by elctronegative atoms.

Both classes of compounds exhibit pyrolytic decomposition and facile hydrolytic cleavage in hot aqueous base. Diphenylphosphinic acid is obtained by either path from both types of compound. The thermal behavior of the *p*-bromophenylcarbamoyl compound indicates a stepwise path proceeding through a higher melting solid.

In the reaction of cyclohexanone and *o*-chlorobenzaldehyde an attempt at "capturing" the suspected intermediate (lithium salt of an α-hydroxy-*t*-phosphine) by reaction with benzyl chloride or bromide to form the benzyl ether of an α-hydroxy-*t*-phosphine resulted in the isolation of sizable amounts of benzyldiphenylphosphine oxide. This compound may have arisen through reaction of the benzyl halide with the type of adduct postulated by Issleib[4] or by reaction with the α-hydroxy-*t*-phosphine salt followed by decomposition or rearrangement.



Since the temperature was never allowed above 40° in the reaction of the benzyl bromide with the adduct of lithium diphenylphosphide and *o*-chlorobenzaldehyde, it seems unlikely that an ether formed by path 1 (see above) should rearrange. Perhaps a mobile equilibrium exists between the "normal" adduct and a coordination complex of lithium diphenylphosphide with the carbonyl compound.



$$Ph_2PLi - - - O{=}C\begin{matrix}R\\ R'\end{matrix} \rightleftarrows Ph_2P-\overset{\overset{Li^{+}}{|\bar{O}|^{-}}}{\underset{R'}{C}}-R$$

Experimental

Preparation of Lithium Diphenylphosphide.—A suspension of 26.2 g. (0.1 mole) of triphenylphosphine, 200 ml. of dry tetrahydrofuran, and 1.4 g. (0.2 g.-atom) of lithium metal strips was stirred rapidly at room temperature under nitrogen for 3 hr., during which time most of the lithium dissolved exothermically producing a deep red solution. The phenyllithium was destroyed by the addition of 9.3 g. (0.01 mole) of *t*-butyl chloride at reflux followed by a 15-min. reflux period. After cooling to ambient temperature, the reaction mass was transferred under a nitrogen atmosphere to a dropping funnel.

Reaction of Carbonyl Compounds with Lithium Diphenylphosphide.[8] **Method A (Normal Addition).**—The solution of lithium diphenylphosphide was added rapidly to a flask under nitrogen, leaving the unchanged lithium in the dropping funnel, and a solution of the carbonyl compound in THF was added dropwise to the refluxing lithium diphenylphosphide solution.

Method B (Inverse Addition).—The solution of lithium diphenylphosphide was added dropwise to a refluxing solution of the carbonyl compound in THF.

Method C (Normal Addition at 20°).—The procedure described under method A was followed, but the lithium diphenylphosphide solution was kept at 20° during the addition.[9]

The color of the phosphide solution was always discharged giving way either to colorless suspension or to a variety of colors depending on the reactant and time after addition. Notable was the final deep blue color obtained in the benzophenone case showing the presence of metal ketyl. After refluxing for 2–3 hr. (except in the case of *o*-chlorobenzaldehyde), the reaction mass was allowed to return to room temperature under nitrogen and then added to 2 l. of water containing 300 ml. of 3% hydrogen peroxide solution.[10] After standing for 12 hr. in some cases a white solid was obtained, while in other cases an oil settled out of the emulsion. After separation from the supernatant aqueous layer, the oil usually yielded the solid product by trituration with ether. Acidification of the basic supernatant aqueous layer led to the precipitation and isolation of diphenylphosphic acid.

Acknowledgment.—We are grateful to Research Corporation and National Science Foundation for their generous support of this work. We wish to thank the Esso Research Center, Linden, New Jersey, for the n.m.r. work on the carbamoyl compounds.

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(8) Method A was used in all cases except that of *o*-chlorobenzaldehyde· Method B was used only in the reaction of cyclohexanone. Method C was used only in the reaction of *o*-chlorobenzaldehyde.

(9) Aryl halides have been found to react with lithium diphenylphosphide: A. M. Aguiar, H. J. Greenberg, and K. E. Rubenstein, *J. Org. Chem.*, **28**, 2091 (1963).

(10) Addition of the reaction mass to an acidic aqueous peroxide solution did not seem to increase the yield of product.

Pyrolysis Studies. IX.[1] Rates and Mechanism of Thermal Decomposition of Phenyl and Benzyl Ethyl Carbonates

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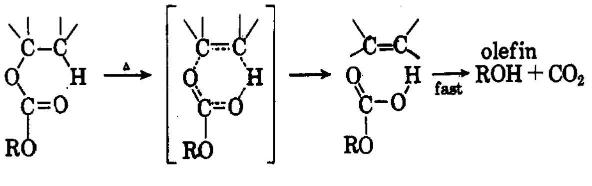
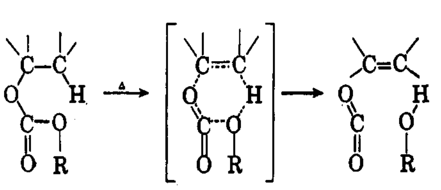
Carbonates containing at least one β-hydrogen atom are known to decompose at elevated temperatures to olefins, alcohols (or phenols), and carbon dioxide.[3] The reaction is first order, shows a negative entropy of activation,[4] and is generally accepted as falling into the category of unimolecular cyclic *cis* eliminations,[5] although this has not been demonstrated experimentally. Two mechanisms have been proposed.



Mechanism I



Mechanism II

Mechanism I[4] postulates initial elimination of the bicarbonate by a mechanism formally similar to that of carboxylic ester pyrolysis. The bicarbonate is then assumed to decompose extremely rapidly to give the alcohol (or phenol) and carbon dioxide, a proposal which is not unreasonable as organic bicarbonates are stable only at low temperatures.[6] Mechanism II[7] shows how all three products could be formed simultaneously.

In a previous publication[8] the decompositions of various ring-substituted phenyl ethyl carbonates and benzyl ethyl carbonates were studied by a gas chromatographic method. The results indicated that the benzyl ethyl carbonates were rather insensitive to the nature of the substituent on the phenyl ring but that the phenyl ethyl carbonates were more sensitive. The per cent decomposition for pyrolysis of phenyl ethyl carbonates for a fixed time decreased slightly with substituent in the order: H > *p*-OMe $\geqslant$ *o*-OMe > *o*-Me > *p*-Me $\geqslant$ *m*-OMe > *m*-Me > *m*-Cl > *p*-Cl > *o*-Cl. This order is rather peculiar as both electronegative *and* electropositive substituents seem to deactivate.

In the present work, absolute rates of decomposition for the vapor phase pyrolysis of series of ring-substituted phenyl and benzyl ethyl carbonates have been determined using a more accurate static method. As expected, the decompositions followed first-order kinetics, in most cases to greater than 90% decomposition (Fig. 1). By changing the surface to volume ratio it was established that the reaction is homogeneous. The results for phenyl ethyl carbonates (Table I) show that the rate of elimination is retarded by electron-releasing substituents attached to the carbonyl group and correspondingly accelerated by electron-withdrawing substituents. This more precise method clarifies the earlier report[8] in which the *o*-, *m*-, and *p*-chlorophenyl ethyl carbonates appeared to decompose slower than the unsubstituted compound.

TABLE I

RATES OF DECOMPOSITION OF SUBSTITUTED PHENYL ETHYL CARBONATES AT 363.4 ± 0.2°

Substituent	$k \times 10^3$, sec.$^{-1}$	Substituent	$k \times 10^3$, sec.$^{-1}$
p-NH$_2$	1.07	3,4-C$_4$H$_4$	1.30
p-OMe	1.13	*o*-Me	1.32
p-*t*-Bu	1.13	*p*-F	1.32
p-Me	1.15	*p*-Cl	1.36
m-Me	1.17	*m*-Cl	1.41
H	1.21	*o*-Cl	1.61
o-OMe	1.23	*p*-NO$_2$	1.67
m-OMe	1.23	*m*-NO$_2$	1.72
p-Ph	1.27	*o*-NO$_2$	3.56

The relative rates are better correlated by Taft's σ^0-values than by the regular Hammett σ-values as shown in Fig. 2.[9] This is exactly as observed in the case of pyrolysis of similarly substituted benzoate esters,[10] and moreover, the ρ-value for the phenyl ethyl carbonate series (0.19) is very close to that observed for a series of ethyl benzoates (0.20).[10]

Although this evidence supports a type I mechanism for elimination, it has not been shown that a type II mechanism would not *also* lead to a σ^0 correlation, so final confirmation must come from other experiments such as a kinetic isotope effect study. In the case of xanthate pyrolysis, in which both stepwise and concerted mechanisms of elimination exactly analogous to the carbonate mechanisms I and II are possible, it has been unequivocally shown by such a kinetic isotope study that the elimination proceeds *via* a type I mechanism.[11,12] This confirmed the postulate of Cram[13] who pointed out previously that a type I mechanism is favored over type II on steric and other theoretical grounds.

The effects of substituent changes in benzyl ethyl carbonate pyrolysis are very small as shown by the results in Table II. The rate data should follow a σ^0 relation, but only the strongly electron-withdrawing *o*-, *m*-, and *p*-chloro, and *o*-, *m*-, and *p*-nitro groups produce any enhancement of rate which is outside of the experimental error. This is understandable as the substituent effects have to be transmitted *via* an extra methylene group; thus the ρ-factor will be much lower than for the phenyl ethyl carbonates. The conclusions from the earlier study[8] are thus largely confirmed with the exception of 'the *o*-methoxybenzyl carbonate, in which the methoxy group was previously thought to show a large activating effect. The enhancement of per cent decomposition seems to have been far greater than could be due to the experimental inaccuracy of the gas chromatographic method, and the

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(1) Part VIII, G. G. Smith and D. A. K. Jones, *J. Org. Chem.*, **28**, 3496 (1963).

(2) (a) Utah State University, Logan, Utah, and to whom inquiries should be addressed; (b) Postdoctoral Research Associate at Utah State University, 1961–1962; (c) Postdoctoral Research Associate at Washinton State University, 1960–1961.

(3) If no β-hydrogen atom is present, decomposition may also occur, but at much higher temperatures and the products are often complex: P. D. Ritchie, *J. Chem. Soc.*, 1054 (1935).

(4) G. L. O'Connor and H. R. Nace, *J. Am. Chem. Soc.*, **75**, 2118 (1953).

(5) C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

(6) W. Hempel and J. Seidel, *Ber.*, **31**, 2997 (1898).

(7) K.-C. Tsou and A. M. Seligman, *J. Am. Chem. Soc.*, **76**, 3704 (1954).

(8) G. G. Smith and B. Kosters, *Ber.*, **93**, 2400 (1960).

(9) σ-Values are from D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958); σ^0-values are from R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

(10) G. G. Smith, D. A. K. Jones, and D. F. Brown, *J. Org. Chem.*, **28**, 403 (1963).

(11) R. F. W. Bader and A. N. Bourns, *Can. J. Chem.*, **39**, 348 (1961).

(12) It may be significant that log $k/k_0{}^0$ values for pyrolysis of a series of *meta*- and *para*-substituted S-benzyl cholesteryl xanthates;[4] when plotted against σ and against σ^0, show less scatter from linearity with the latter.

(13) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3883 (1949).

most likely explanation is that some free-radical decomposition was occurring. The precautions taken to eliminate such complications in the present study are described in the experimental section. The results for these and other *ortho*-substituted carbonates will be discussed in more detail in a subsequent paper dealing with polar effects of *ortho* substituents in gas phase reactions.

TABLE II

RATES OF DECOMPOSITION OF SUBSTITUTED BENZYL ETHYL CARBONATES AT 384.5 ± 0.2°

Substituent	$k \times 10^3$, sec.$^{-1}$	Substituent	$k \times 10^3$, sec.$^{-1}$
o-OMe	2.57	*m*-Cl	2.83
m-OMe	2.57	*p*-Cl	2.84
H	2.63	*o*-Cl	2.90
p-Me	2.64	*p*-NO_2	2.98
o-Me	2.67	*m*-NO_2	3.04
m-Me	2.67	*o*-NO_2	6.49
p-OMe	2.69		

Experimental

Carbonate Preparation.—Except where mentioned, the carbonates were prepared from the commercially available phenols or benzyl alcohols using ethyl chloroformate as described previously.[8] Compounds were carefully purified and stored in the dark under refrigeration to preclude formation of free radicals and minimize decomposition. The physical constants and yields of compounds not recorded in the earlier paper[8] are given in Table III.

TABLE III

PHYSICAL CONSTANTS AND YIELDS OF PHENYL AND BENZYL ETHYL CARBONATES

Ethyl carbonate	Yield, %	M.p. or b.p. (mm.), °C.	$n^{20}D$	Empirical formula	Analyses[a] Calcd., % C	H	N	Found, % C	H	N
p-Aminophenyl	53	124 (0.02)	1.5333	$C_9H_{11}NO_3$	59.66	6.12	7.73	58.99	5.97	7.62
p-*t*-Butylphenyl	86	94–96 (0.5)	1.4890	$C_{13}H_{18}O_3$	70.24	8.16		70.17	8.02	
p-Fluorophenyl	86	70 (1.4)	1.4709	$C_9H_9FO_3$	58.70	4.93	10.32[b]	58.59	4.99	10.57[b]
o-Nitrophenyl	66	15.5, 116–118 (0.8)[c]	1.5164	$C_9H_9NO_5$	51.19	4.30	6.63	51.42	4.30	6.76
m-Nitrophenyl	72	52.5–53,[d] 130–131 (1.8)		$C_9H_9NO_5$	51.19	4.30	6.63	51.55	4.08	6.69
p-Nitrophenyl	77	68[e]								
p-Phenylphenyl	55	74–74.5[f]								
β-Naphthyl	38.5	33–33.8[g]								
o-Nitrobenzyl	70	42[h]		$C_{10}H_{11}NO_5$	53.32	4.92	6.22	53.24	4.92	6.54
m-Nitrobenzyl	78	35, 149–151 (1.6)		$C_{10}H_{11}NO_5$	53.32	4.92	6.22	53.55	4.82	6.32
p-Nitrobenzyl	50	91.5–92[i]		$C_{10}H_{11}NO_5$	53.32	4.92	6.22	53.13	4.84	6.45

[a] Analyses by A. Bernhardt, Mülheim (Ruhr), Germany. [b] % F. [c] Lit. b.p. 275–285° dec. [G. Bender, *Ber.*, **19**, 2265 (1886)]. [d] Recrystallized from petroleum ether (b.p. 30–60°). [e] Lit. m.p. 67–68° [J. H. Ransom, *Ber.*, **31**, 1955 (1898)]. [f] Lit. m.p. 73.9–75.0° [E. Baumgarten, H. G. Walker, and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 303 (1944)]. [g] Lit. m.p. 34–35° [M. Harfenist and R. Baltzly, *ibid.*, **69**, 362 (1947)]. [h] Recrystallized from petroleum ether (b.p. 60–90°). [i] Recrystallized from ethanol.

Ethyl *p*-Aminophenyl Carbonate.—Ethyl *p*-nitrophenyl carbonate (11 g.) was dissolved in absolute ethanol, Adam's catalyst (0.5 g.) was added, and the mixture was hydrogenated at room temperature at 35 p.s.i. for 4 hr., in a Parr pressure reaction apparatus. The reaction mixture was filtered, the ethanol was removed, and the product was fractionated under reduced pressure.

Method of Pyrolysis.—The method of pyrolysis and the apparatus have been described.[1,14] In some cases the pressure changes were followed manually, in others the automatic system was used. All compounds were injected in a 1:1 chlorobenzene or cyclohexene solution with a hypodermic syringe. Particular precaution was taken to avoid any trace of a wall reaction and only data from a well seasoned reactor was used. In order to safeguard against activating the reactor by introducing oxygen into the evacuated system, a toy balloon filled with pure nitrogen was attached around the end of the syringe. The reaction temperature was 363.4 ± 0.2° for the phenyl ethyl carbonates and 384.5 ± 0.2° for the benzyl ethyl carbonates. The surface to volume ratio was increased 10 times by inserting a stainless steel sponge inside the reaction vessel. After complete deactivation of the new surface the rate of the *m*-methoxyphenyl ethyl carbonate was found to be 1.38 × 10^{-3} sec.$^{-1}$ at 364.0 ± 0.2° and 1.83 × 10^{-3} sec.$^{-1}$ at 365.0 ± 0.2° as compared to the value of 1.23 × 10^{-3} sec.$^{-1}$ at 363.4 ± 0.2° in the unpacked reactor.

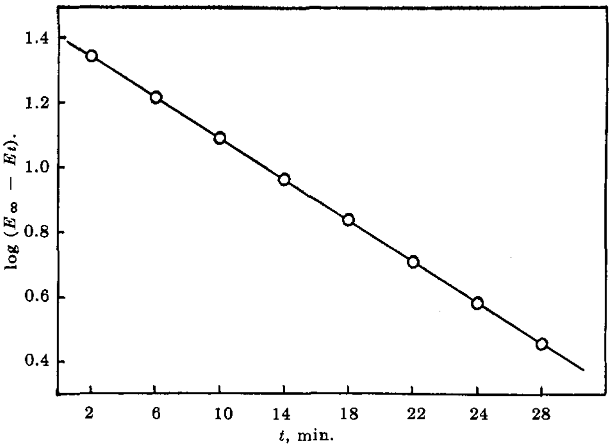

Fig. 1.—First-order rate constant for the pyrolysis of phenyl ethyl carbonates to greater than 90% reaction.

The *o*-nitrophenyl ethyl carbonate gave a first-order plot to greater than 75% decomposition giving a rate of 3.80 × 10^{-3} sec.$^{-1}$ at 365.8 ± 0.2° in a packed reactor compared to 3.56 × 10^{-3} sec.$^{-1}$ at 363.4 ± 0.2° in the unpacked reactor.

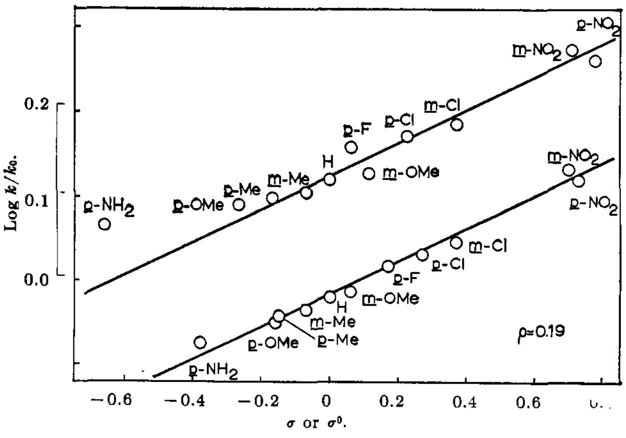

Fig. 2.—Hammett σ plot (upper) and Taft σ^0 plot (lower) for pyrolysis of substituted phenyl ethyl carbonates.

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(14) (a) G. G. Smith and F. D. Bagley, *Rev. Sci. Inst.*, **32**, 703 (1961); (b) G. G. Smith, F. D. Bagley, and R. Taylor, *J. Am. Chem. Soc.*, **83**, 3647 (1961).

Calculation of Rate Constants.—With the exception of the nitrophenyl and nitrobenzyl ethyl carbonates, first-order rate constants were obtained from the slopes of the plots of log ($P_\infty - P_t$) or log ($E_\infty - E_t$) against time. The nitro compounds showed secondary decomposition, and their first-order rate constants were obtained from the initial slopes of plots of dE/dt against E.[1] The phenyl ethyl carbonates were all pyrolyzed several times, and the mean values of the rate constants are given in Table I. Average deviations from the mean were within ±1% except for the *p*-methoxy compound (±1.5%). The precision in the pyrolysis of benzyl ethyl carbonates was *ca.* ±2%. Rate constants are given in Table II.

Acknowledgment.—This work was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Grant No. AF-AFOSR 62-268 and Contract No. AF 49(638)616. Acknowledgment also is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Utah State University Division of University Research for partial support of this research.

We are grateful to Dr. B. Kösters, Mr. V. R. Rice, and Mr. D. V. White for assistance with synthetic work, and to Mr. J. A. Kirby for some of the rate data.

Autoxidation of Galvinoxyl[1]

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Received July 1, 1963

The hindered phenoxyl radical galvinoxyl,[2] G·, [derived from 2,6-di-*t*-butyl-4-(3,5-di-*t*-butyl-4-hydroxybenzal)cyclohexadienone] is finding increasing use as a radical scavenger.[3] The original reports[2] indicated that it was stable to oxygen both in the solid phase and in solution. We wish to call attention to the instability of solutions of galvinoxyl and to the interesting feature of its consumption *via* an autocatalytic path: A freshly prepared solution of galvinoxyl (10^{-3} M) in undegassed benzene at 25° was observed to undergo almost no change in optical density for many minutes, after which induction period the concentration of galvinoxyl rapidly fell. This behavior also took place in the dark but did not occur in degassed solvent. When a solution of galvinoxyl was shaken in an atmosphere of oxygen, the rate of disappearance of galvinoxyl (followed spectrophotometrically) closely paralleled the rate of uptake of oxygen (Fig. 1). Oxygen consumption was 1.4 moles per mole of galvinoxyl. Among the oxidation products were 2,6-di-*t*-butyl-1,4-benzoquinone (20%) and 3,5-di-*t*-butyl-4-hydroxybenzaldehyde (4%). No other discrete products were isolated from the residual tar.

A number of experiments were effected to ascertain the basis of the inhibition period. Autocatalysis by products of the autoxidation reaction was excluded in that the addition of fresh galvinoxyl to an already oxidized solution exhibited a similar induction period. In view of the general effectiveness of phenols as inhibitors of autoxidation, a small sample of the bisphenol trihydrogalvinoxyl, GH_3 (3,5,3′,5′-tetra-*t*-butyl-4,4′-dihydroxydiphenylmethane), was added to a solution of galvinoxyl in benzene. An inmediate reaction occurred, and the remaining galvinoxyl *was markedly stabilized towards oxygen* (Fig. 2). The stoichiometry of the galvinoxyl-*tri*hydrogalvinoxyl reaction[4] is 2:1, producing hydrogalvinoxyl, GH, in high yield.

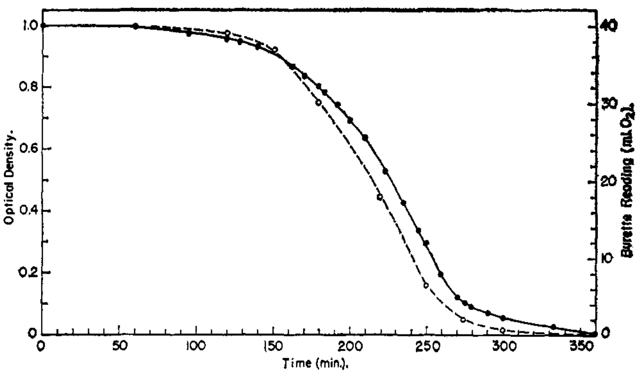
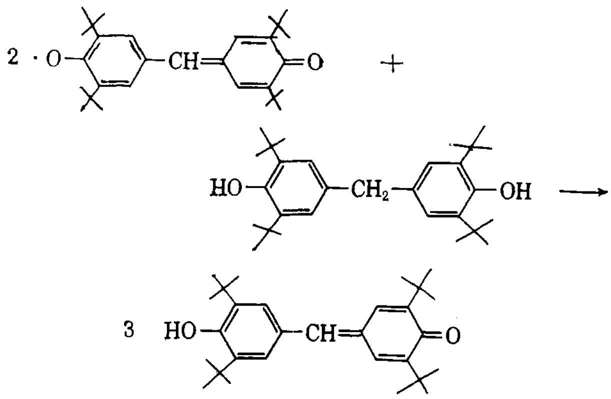


Fig. 1.—Autoxidation of galvinoxyl (0.02 M) in benzene by shaking in an oxygen atmosphere at room temperature: solid circles, consumption of oxygen; open circles, consumption of galvinoxyl followed spectrophotometrically at 530 mμ.



The data of Fig. 2 are suggestive that the inhibition period, Fig. 1, is due to the presence of hydrogalvinoxyl, an impurity difficult to remove in the preparation of galvinoxyl. The addition of hydrogalvinoxyl to a solution of galvinoxyl revealed a close relationship between the amount added and the length of the inhibition period (Table I). These data are suggestive of the presence of a few per cent of hydrogalvinoxyl in the galvinoxyl (in accord with the value of 97 ± 1% purity determined by the titrimetric method) and carry the further implication that a completely pure sample of galvinoxyl in solution might undergo rapid autoxidation.

The inhibition period is also markedly dependent on concentration. A 10^{-3} M solution of galvinoxyl in benzene was 50% consumed in 1 hr.; a 4×10^{-6} M solution was only 10% destroyed in 24 hr. The sta-

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(1) This work was supported by the research program of the Atomic Energy Commission under Contract No. AT(30-1)-905. Reproduction is permitted for any purpose of the U. S. Government.

(2) (a) G. M. Coppinger, *J. Am. Chem. Soc.*, **79**, 501 (1957); (b) M. S. Kharasch and B. S. Yoshi, *J. Org. Chem.*, **22**, 1435 (1957).

(3) (a) P. D. Bartlett and T. Funahashi, *J. Am. Chem. Soc.*, **84**, 2596 (1962); (b) P. D. Bartlett, B. H. Gontarev, and H. Sakurai, *ibid.*, **84**, 3101 (1962); (c) F. D. Greene, W. Adam, and J. E. Cantrill, *ibid.*, **83**, 3461 (1961).

(4) The reaction kinetics is complex. It is hoped that a full account of the G-GH_3 reaction can be presented at a later date.