yellow color persisted for 2 minutes. Excess diazomethane and ether was then boiled off and the ester used for epimerization without purification.

Epimerization of Xa to Xb.—To a solution of 90 mg. of sodium in 10 ml. of absolute ethanol was added 180 mg. of methyl ester of Xa, and the solution was refluxed for 24 hours. Water (5 ml.) was then added dropwise and the mixture was refluxed for an additional 4 hours. The reaction mixture was then diluted with 10 ml. of water and thoroughly washed with ether. The aqueous layer was then acidified with 5 N hydrochloric acid and the precipitate which formed was collected by filtration and dried under vacuum. This was then sublimed (58°; 0.8 mm.) to give 45 mg. of oily liquid which gave an infrared spectrum identical with that of Xb. This oily liquid was dissolved in 5% NaOH and was reprecipitated by acidification with 5 N hydrochloric in a white, crystalline state, m.p. 58°. This product showed no depression in m.p. when mixed with Xb. It gave an infrared spectrum identical with that of Xb.

Preparation of Iodolactone XI.—A solution of 508 mg. (0.004 mole) of iodine and 2 g. of potassium iodide in 6 ml. of water was added to 248 mg. (0.002 mole) of IXa dissolved in 12 ml. of 0.5 N sodium bicarbonate solution. The mixture was allowed to stand in the dark at room temperature for 24 hours. A light yellow crystalline product formed and was separated by filtration and air-dried. It amounted to 380 mg. (76%), m.p. 97–102°. The infrared spectrum of the crude product showed it to be mainly δ-lactone (5.75 μ) containing a small amount of the γ-lactone (5.65 μ). The δ-lactone, m.p. 105.5°, was obtained in pure state by crystallization from cyclohexane; infrared (CHCl₃): 5.75, 6.95, 7.26, 7.37, 7.50, 8.69, 9.11, 9.23, 9.53, 9.80, 10.00, 10.28, 10.47, 11.24, 11.58, 11.91 μ.

Anal. Calcd. for C₇H₇O₂I: C, 33.60; H, 2.80; I, 50.80. Found: C, 33.42; H, 2.82; I, 50.86.

Conversion of Iodolactone XI to Acid IXa.—Iodolactone XI (90 mg.) was dissolved in 30 ml. of glacial acetic acid and cooled to

5°. Zinc dust (400 mg.) previously cooled to 5° was dropped at once into the iodolactone solution. The mixture was vigorously shaken for 5 minutes and quickly filtered through a bed of Celite (prepared by suspending Celite in acetic acid, filtering and washing with acetone). Acetic acid was removed under vacuum and the residue was dissolved in sodium hydroxide solution, extracted with chloroform and acidified with 5 N hydrochloric acid. The solution was extracted three times with ether. The ethereal layer was dried over anhydrous sodium sulfate and the ether removed on the flash evaporator. The product was purified by crystallization from hexane to give 25 mg. (55%) of pure acid, m.p. 90–91°, which showed no depression in mixed melting point with IXa and gave an infrared spectrum identical with that of IXa.

Vapor Phase Chromatography.—Vapor phase chromatography was carried out using a Beckman GC-2 instrument equipped with a 6-ft. Craig polyester column at 160°. Helium at a pressure of 20 p.s.i. was used as carrier gas.

Compound	Retention time, min.
Methyl bicyclo[3.1.0]hex-2-ene-*endo*-6-carboxylate	13.5[a]
Methyl bicyclo[3.1.0]hexane-6-*endo*-carboxylate	11.0[a]
Methyl cyclohexanecarboxylate	7.8[a]
Methyl bicyclo[3.1.0]hexane-6-*exo*-carboxylate	13.5[a]
Pd–C prod. from hydrogenation of IXa	7.8 (1st peak) 11.0 (2nd peak) 19.7 (3rd peak)

[a] No detectable impurity.

Decomposition Reactions of Alkyl Chloroglyoxalates[1,2]

BY SARA JANE RHOADS AND ROBERT E. MICHEL[3]

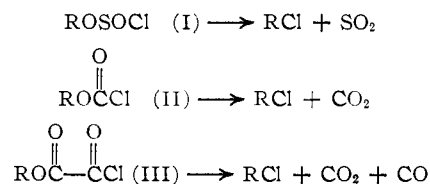RECEIVED SEPTEMBER 10, 1962

Alkyl chloroglyoxalates of structure ROCOCOCl (R = C₂H₅, *n*-C₄H₉, 2-C₈H₁₇, C₆H₅CHCH₃) decompose smoothly when heated in the presence of pyridine to yield the corresponding alkyl chlorides, carbon dioxide and carbon monoxide. The decompositions of active 2-octyl chloroglyoxalate (IIIc) and active α-phenethyl chloroglyoxalate (IIId) have been studied as pyridine-induced reactions and as thermal reactions. Both IIIc and IIId undergo the pyridine-induced decomposition to give the corresponding alkyl chlorides with a high degree of inversion of configuration, a result suggestive of an SN2 process involving the first-formed pyridinium salt. Compound IIIc is resistant toward decomposition when heated alone or in neutral solvents, while IIId decomposes when heated alone or in nitrobenzene to give α-phenethyl chloride with a preponderance of retention of configuration. Relative rates of the first-order thermal decomposition of IIId in tetralin, diglyme and nitrobenzene are 1:2.34:13.6 at 108°. In comparison with the structurally analogous alkyl chloroformates and alkyl chlorosulfinates, the alkyl chloroglyoxalates show an unexpected thermal stability. The mechanistic implications of these findings for the thermal decomposition are discussed in terms of current hypotheses concerning SNi reactions.

Although the advantages of oxalyl chloride as a reagent for the conversion of acids to acid chlorides have been recognized for many years,[4] its potentiality as a reagent for the corresponding conversion of alcohols to alkyl chlorides appears to have been neglected.[5] In order to explore the possible use of oxalyl chloride for the preparation of alkyl chlorides and also to compare it with reagents more commonly used for this purpose, *e.g.*, thionyl chloride and phosgene, a number of alkyl chloroglyoxalates (III) have been prepared and studied with respect to their decomposition behavior.

The structural parallelism among the alkyl chlorosulfinates I, the alkyl chloroformates II and the alkyl

chloroglyoxalates III led to the expectation that the last would suffer facile decomposition with the formation of an alkyl chloride, carbon dioxide and carbon monoxide. Moreover, it was anticipated that the decomposition of III would respond, ratewise and stereochemically, to changes in intra- and extramolecular environment in much the same manner as do the structural analogs I and II.[6] Finally, on the basis of alkyl–

$$\text{ROSOCl} \quad (\text{I}) \longrightarrow \text{RCl} + \text{SO}_2$$

$$\underset{\text{ROCCl}}{\overset{\text{O}}{\|}} \quad (\text{II}) \longrightarrow \text{RCl} + \text{CO}_2$$

$$\underset{\text{ROC—CCl}}{\overset{\text{O} \quad \text{O}}{\| \quad \|}} \quad (\text{III}) \longrightarrow \text{RCl} + \text{CO}_2 + \text{CO}$$

oxygen bond strengths, it was expected that the alkyl chloroglyoxalates would show a thermal stability inter-

(4) R. Adams and L. H. Ulich, *J. Am. Chem. Soc.*, **42**, 599 (1920).

(5) R. Adams and co-workers, *ibid.*, **37**, 2716 (1915); **38**, 2514 (1916); **40**, 424 (1918), studied the reactions of oxalyl chloride with hydroxylic reagents as preparative routes to esters and olefins.

(6) Summarizing discussions may be found in E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt–Dryden, New York, N. Y., 1959, p. 294, and J. Hine, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1956, p. 114.

TABLE I

DECOMPOSITION OF ALKYL CHLOROGLYOXALATES IN THE PRESENCE OF PYRIDINE

$$\underset{C_5H_5N}{\overset{O\ \ O}{\underset{\Delta}{ROC\!-\!CCl \longrightarrow}}} RCl + \text{olefin} + CO + CO_2$$

R	T, °C.	Time, hr.	Gas evolved % theory	Yield, % (RCl + olefin)	Product composition[a] RCl	Olefin
C₂H₅	110 ± 10	3.0	90	..[b]	C₂H₅Cl	........[c]
n-C₄H₉	125 ± 10	3.5	95	60	n-C₄H₉Cl	........[c]
2-C₈H₁₇	100 ± 10	6.0	96	60	2-C₈H₁₇Cl, 85–88%	2-Octene, 12–15%
PhCHCH₃	100 ± 10	5.5	92	11	PhCHClCH₃, 90–95%	PhCH=CH₂, 5–10%
PhCHCH₃	69[d]	10.0	..[e]	51	PhCHClCH₃, 100%	None

[a] By g.l.p.c. analysis. [b] Yield not determined. [c] No attempt was made to trap olefin in this case. [d] Reaction carried out in refluxing carbon tetrachloride. [e] The progress of the reaction was followed by g.l.p.c. analysis of the reaction mixture; in 10 hours, the reaction was 80% complete.

mediate to those of the chlorosulfinates and the chloroformates.[7]

Results

The alkyl chloroglyoxalates III are readily prepared by simply combining equimolar quantities of oxalyl chloride and the appropriate alcohol. The reactions proceed rapidly at room temperature when the alcohol is added dropwise to the stirred oxalyl chloride. Distillation of the reaction mixture affords the alkyl chloroglyoxalate as a middle fraction in yields of 60–70%. In this manner, ethyl (IIIa), n-butyl (IIIb), 2-octyl (IIIc) and α-phenethyl chloroglyoxalate (IIId) have been prepared. The properties of these substances are recorded in the Experimental section.

$$\underset{\text{IIIa, R = C}_2\text{H}_5}{\overset{O\ \ O}{ROH + ClC\!-\!CCl \longrightarrow ROC\!-\!CCl + HCl}}$$

b, R = n-C₄H₉
c, R = CH₃CHC₆H₁₃
d, R = C₆H₅CHCH₃
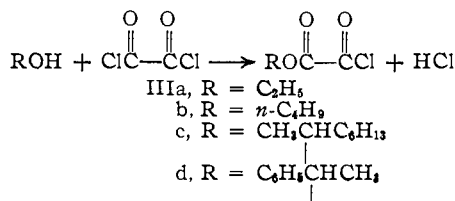
In order to confirm the predicted decomposition pattern, attention was first directed to the behavior of the alkyl chloroglyoxalates when heated in the presence of pyridine. Typical results are summarized in Table I. At bath temperatures of 100–125° the pyridine-induced decompositions of the alkyl chloroglyoxalates take place smoothly with the formation of the expected products. The decompositions were followed by collection of evolved gases. Product analysis and identification were made by gas–liquid partition chromatography (g.l.p.c.) of the isolated products.

In each case, the addition of pyridine to the alkyl chloroglyoxalate was marked by the formation of a voluminous white precipitate. This solid, presumably the pyridinium salt of the chloroglyoxalate, slowly disappeared during the course of the reaction. Complete decomposition of the chloroglyoxalates occurred only in the presence of an equivalent amount of pyridine; when catalytic amounts of the base were used, a solid sublimate of pyridine hydrochloride began to appear in the condenser soon after decomposition began. Coincident with the removal of pyridine from the reaction mixture in this manner, the decomposition diminished in rate and finally stopped entirely. This effect was most pronounced in the decomposition of the

secondary alkyl derivatives IIIc and IIId where concurrent olefin (and hydrogen chloride) formation is appreciable.

The low yield and the difficulty encountered in the isolation of the products from the pyridine-induced decomposition of the α-phenethyl compound IIId are attributed to diversion of the product by dehydrohalogenation and subsequent polymerization. The use of carbon tetrachloride as a solvent (Table I) obviated this trouble.

The stereochemical outcome of the pyridine-induced decomposition of the alkyl chloroglyoxalates was determined by the study of IIIc and IIId in active form (Table II). The alkyl chloroglyoxalates were prepared

TABLE II

PYRIDINE-INDUCED DECOMPOSITION OF ACTIVE ALKYL CHLOROGLYOXALATES

R	[α]²⁵D ROH	Solvent	[α]²⁵D RCl	Stereochemical outcome
2-C₈H₁₇	− 9.54°	None	+33.7°[a]	Inversion
PhCHCH₃	−22.7°	CCl₄	+53.4°	Inversion

[a] Corrected for olefin content; see Experimental.

from active alcohols of the rotations shown in the table. The active 2-octyl chloroglyoxalate (IIIc) had an observed rotation of the same sign and 2.55 times that of the alcohol from which it was prepared. The active α-phenethyl chloroglyoxalate (IIId) showed an observed rotation of the same sign and 2.40 times that of the alcohol from which it was made. Basic hydrolysis of the active chloroglyoxalates IIIc and IIId regenerated the original alcohols without change in activity, thereby establishing configurational identity in the alcohols and the corresponding chloroglyoxalates. The results of the decompositions of (−)-IIIc and (−)-IIId, shown in Table II, characterize the pyridine-induced process as a strongly inverting one. Calculations based on the highest values reported for the activities of the pertinent alcohols and alkyl chlorides suggest that the decomposition of IIIc proceeds with at least 95.4% inversion and that of IIId with 85.8 (min.) to 98.5% (max.) inversion.[8–11]

(7) Such an expectation is based on the assumption that the rate-determining step involves heterolysis of the alkyl–oxygen bond and upon the

relative stabilities of the anions so formed, i.e., ⁻O–C–Cl < ⁻O–C–C–Cl ≪ ⁻OSOCl. The latter order of stabilities may be inferred from Kₐ's of related acids, i.e., HCOOH, Kₐ = 18 × 10⁻⁵; HCOCOOH, Kₐ = 47 × 10⁻⁵; C₂H₅SO₃H, Kₐ = 3.1 × 10⁻³.

(8) R. N. Pickard and J. Kenyon, J. Chem. Soc., 99, 45 (1911), give [α]¹⁷D ±9.90° (neat) for optically pure 2-octanol.

(9) H. Brauns, Rec. trav. chim., 65, 799 (1946), reports [α]²⁰D ±36.14° (neat) for optically pure 2-chloroöctane.

(10) The rotation of optically pure α-phenethyl alcohol is given as [α]²⁵D ±43.4° (neat) by A. McKenzie and G. W. Clough, J. Chem. Soc., 103, 687 (1913).

(11) The rotation of optically pure α-phenethyl chloride is not known. A maximum value of [α]²⁵D ±119° (neat) has been calculated by R. L. Buswell, A. D. Shields and H. Hart, J. Am. Chem. Soc., 76, 908 (1954) [see also H. Hart and H. S. Eleuterio, ibid., 76, 516 (1954)], although chloride of this optical purity has not been obtained. The highest observed stereospecificity in the conversion of α-phenethyl alcohol to the chloride was re-

In view of the thermal lability reported for *sec*-alkyl chlorosulfinates[12] and chloroformates,[13] the relative stability of corresponding alkyl chloroglyoxalates was unexpected. Only with α-phenethyl chloroglyoxalate (IIId) could an uncatalyzed, thermal decomposition be realized. The 2-octyl chloroglyoxalate (IIIc) is remarkably stable, resisting decomposition when heated alone to 200–250° or when heated for long periods in a variety of high-boiling solvents. It may even be distilled at atmospheric pressure with very little evidence of decomposition. Similar stabilities are noted for the ethyl and *n*-butyl chloroglyoxalates.

The thermal decomposition of α-phenethyl chloroglyoxalate (IIId) was investigated in the absence of solvent and in the presence of solvents of varying ionizing power. Table III summarizes the results. The reactions in diglyme and in tetralin were followed to

TABLE III

THERMAL DECOMPOSITION OF α-PHENETHYL CHLOROGLYOXALATE

Solvent	Temp., °C.	Product composition[a] Chloride	Olefin	Stereochemical results $[\alpha]^{25}$D ROH	$[\alpha]^{25}$D RCl
None	125	60	40	−16.60°	− 3.62[ob]
Nitrobenzene	108	90	10	−16.60°	−16.45[oc]
Diglyme[d]	150	75	25	......	....
Tetralin	110	80	20	......	....

[a] By g.l.p.c. analysis of the reaction mixture. [b] Corrected for olefin content; see Experimental. [c] Rotation measured in nitrobenzene; see Experimental. [d] Bis-(2-methoxyethyl) ether.

only 40–50% completion while those in nitrobenzene and the absence of solvent were essentially complete as shown by g.l.p.c. analysis of the reaction mixture. That the olefin is a primary product of the thermal decomposition was shown by the fact that when α-phenethyl chloride was heated alone or in nitrobenzene solution under simulated reaction conditions less than 1% styrene was produced. The stereochemical results for the decompositions in the absence of solvent and in nitrobenzene are shown in the last column of Table III. When active IIId, prepared from alcohol of $[\alpha]^{25}$D −16.60° (neat), was decomposed by heating in nitrobenzene at 108° for 14 hours (∼10 half-lives), the isolated chloride showed a specific rotation of −16.45° (nitrobenzene, *c* 28), a result which corresponds to 57.0% (min.) to 65.4% (max.) retention of configuration and 43.0% (max.) to 34.6% (min.) racemization.[11] In the absence of solvent, racemization was much more extensive although retention was still apparent; the chloride, which was isolated by continuous removal from the reaction flask held at 125° under 40 mm. pressure, showed $[\alpha]^{25}$D −3.62° (neat), or 90.9 (min.) to 92.1% (max.) racemization.

Since the more extensive racemization was accompanied by larger amounts of olefin in the product mixture, it seemed likely that at least part of the racemization could be accounted for by the action of hydrogen chloride on the active chloride subsequent to its formation. This possibility was checked by heating samples of active α-phenethyl chloride in nitrobenzene containing hydrogen chloride under simu-

ported by these same authors, who used phosphorus oxychloride and pyridine as reagents. The chloride obtained in this way had a specific rotation $[\alpha]^{25}$D 103.6° (neat) or a (specific) rotation 2.38 times that of the alcohol used (predicted ratio for 100% stereospecific conversion is 2.74). Viewed in the same way, the pyridine-induced decomposition of α-phenethyl chloroglyoxalate gives chloride with a rotation 2.35 times that of the starting alcohol. The ranges given for the stereochemical results in the α-phenethyl series in this paper are based on the limits established by Hart, *et al.*, *i.e.*, $[\alpha]^{25}$D ±103.6° (minimum) and $[\alpha]^{25}$D ±119° (maximum).

(12) (a) E. S. Lewis and C. E. Boozer, *J. Am. Chem. Soc.*, **74**, 308 (1952); (b) C. E. Boozer and E. S. Lewis, *ibid.*, **75**, 3182 (1953).

(13) (a) A. J. H. Houssa and H. Phillips, *J. Chem. Soc.*, 108 (1932); (b) M. B. Harford, J. Kenyon and H. Phillips, *ibid.*, 179 (1933); (c) K. B. Wiberg and T. M. Shryne, *J. Am. Chem. Soc.*, **77**, 2774 (1955).

lated reaction conditions. When a solution 0.36 *M* in α-phenethyl chloride and 0.05 *N* in hydrogen chloride was held at 108° for 10 hours, a loss of rotation corresponding to 9.84% racemization was observed. This value may be taken as the minimum amount of racemization attributable to the presence of hydrogen chloride in the decomposition reaction mixture since the mole ratio of alkyl chloride to hydrogen chloride (7.2:1) corresponds to the alkyl chloride–styrene mole ratio of the reaction product as determined by g.l.p.c.[14] In fact, however, the concentration of hydrogen chloride in the reaction mixture during the heating period could have been considerably higher than 0.05 *N* since some (unknown) portion of the concurrently produced styrene could have been diverted to polymeric material during the decomposition period. In order to establish an upper limit to the HCl-induced racemization, a parallel experiment was conducted in a nitrobenzene solution which was saturated with hydrogen chloride at 108° (0.12 *N*). Under these conditions, a total racemization of 49.5% in 10 hours was realized. This result clearly overcorrects for the HCl-induced racemization and the true correction value lies somewhere between the extremes. If the activity of the α-phenethyl chloride is corrected for the minimum amount of HCl-induced racemization, the corrected rotation of $[\alpha]^{25}$D −18.25° (nitrobenzene, *c* 28) corresponds to 63.3% (min.) to 72.6% (max.) retention of configuration and 36.7% (max.) to 27.4% (min.) racemization. It is apparent, then, that the thermal decomposition of IIId in nitrobenzene does proceed with a high degree of retention of configuration but that this fact is somewhat obscured by subsequent racemization under the reaction conditions.

Further information concerning the nature of the thermal decomposition of α-phenethyl chloroglyoxalate was obtained from a series of rate studies in three solvents. The decompositions were followed by the volumetric measurement of the evolved gases (CO_2 and CO) and showed excellent first-order behavior throughout the ranges studied. In the faster reactions, the decompositions were followed to 70–80% completion. Table IV contains a summary of rate constants;

TABLE IV

FIRST-ORDER REACTION RATE CONSTANTS FOR THE DECOMPOSITION OF α-PHENETHYL CHLOROGLYOXALATE

Solvent	T, °C.	$k \times 10^5$, sec.$^{-1}$[a]	$k/k_{tetralin}$
Tetralin	108.3	0.998 ± 0.017	1.00
Diglyme	108.3	2.34 ± .18	2.34
Nitrobenzene	97.5	6.17 ± .18	
	108.3	13.6 ± .12	13.6
	117.4	26.5 ± .50	
	121.9	30.2 ± .80	

[a] Uncertainties are average deviations of at least three runs.

sample rate data are recorded in the Experimental section. From rate measurements in nitrobenzene at four temperatures, the activation quantities $\Delta H^{\ddagger}_{381.4}$ = 19.0 ± 1 kcal./mole and $\Delta S^{\ddagger}_{381.4}$ = − 27 ± 2 e.u. were evaluated.

Discussion

The gross mechanistic picture derived from these studies for the decompositions of the alkyl chloroglyoxalates IIIc and IIId parallels that generally envisaged for halide formation from demonstrated or assumed ester–halide intermediates.[6] Thus, for the

(14) In the decomposition experiment on the active chloroglyoxalate, the reaction mixture was held at 108° for 14 hours, or 10 half-lives. By the end of the first 4 hours, the reaction was approximately 86% complete and the racemization process well underway. Thus, the total amount of racemization achieved in the 14-hour reaction period is minimally approximated by the racemization experiment conducted over a 10-hour period.

pyridine-induced decompositions, a reasonable sequence is that shown in eq. 1. Preliminary formation of the pyridinium salt IV liberates a chloride ion which, in turn, may initiate SN2 displacement at the active center, a series of events consonant with the strongly inverting nature of the reaction. Alternatively, external chloride ion may be available from a concurrent elimination process.

$$\text{(1)}$$
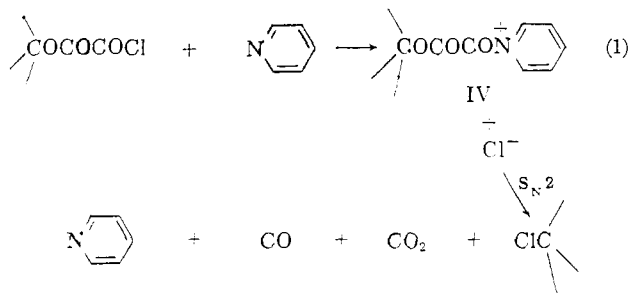
The preponderance of retention of configuration in the thermal decomposition of active α-phenethyl chloroglyoxalate speaks for an internal process of the SNi type (eq. 2) as a major reaction pathway in this case just as in the corresponding chlorosulfinate and chloroformate cases. The electronic nature of such internal processes has been discussed by numerous investigators[15] in recent years and it is generally agreed that between the mechanistic extremes of the cyclic covalent process A and the ion-pair process B there lies a graded continuum of such reactions. Clear-cut distinctions between the essentially covalent and the predominantly ionic processes are, as a consequence of this merging pattern, experimentally difficult. Nonetheless, efforts have been made to detect the differences, at least at the extremes of the mechanistic spectrum. Two criteria have commonly been applied: the effect of substituents on the carbon undergoing substitution and the effect of solvent. Both of these effects may be gaged by the magnitude of the rate differences within a systematically varied series.

$$\text{(2)}$$
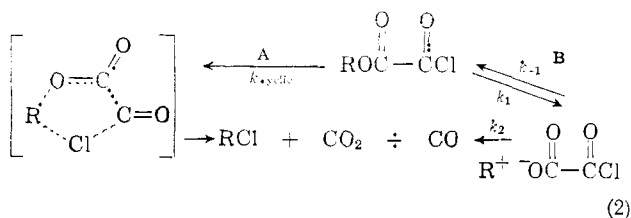
Thus, Wiberg and Shryne[13c] interpreted the large negative ρ-values found in their $\rho\sigma$-correlation of the decomposition of p-substituted α-phenethyl chloroformates as evidence for the intervention of tight ion-pair intermediates in these decompositions. Similarly, the correlation of reactivity and stability of the (incipient) carbonium ion has been advanced as evidence for a rate-determining heterolysis of the C–O bond in alkyl chlorosulfinates and chloroformates.[15c,d] The use of rate response to solvent ionizing power has been advocated by Winstein as a still more sensitive method for differentiating ion-pair processes and nonionic cyclic processes, and a scale of relative solvent ionizing power has been introduced.[16] Applying this criterion in their study of the decomposition of α-methylallyl chloroformate, Olivier and Young[15d] found

a rate factor of $ca.$ 10,000 for a solvent change from decane to nitrobenzene, a result which, by its very magnitude, seems to demand an ionic process. In contrast, for the thermal decomposition of α-trifluoroallyl chlorosulfinate, Pegolotti and Young[17] found a rate response of only sevenfold with a solvent change from decane to nitrobenzene and concluded that the decomposition of this chlorosulfinate was of the cyclic, covalent type. Similar insensitivity to solvent ionizing power has been observed and taken as evidence for the absence of ionic processes in the thermal rearrangements of allylic thiobenzoates[13a] and allylic azides.[18b]

Although the present work does not allow an assessment of the magnitude of the effect of structural variation in the alkyl group of the substrate, it is clear that the ease of thermal decomposition of the alkyl chloroglyoxalates does increase with increasing carbonium ion stability as qualitatively demonstrated by the difference in the thermal stabilities of the 2-octyl and α-phenethyl derivatives. On the other hand, the solvent response of the thermal decomposition of α-phenethyl chloroglyoxalate is a relatively low one when compared with that of α-methylallyl chloroformate. Thus, Olivier and Young[15d] found a rate ratio of $ca.$ 100:1 for the chloroformate decomposition in the solvents nitrobenzene and toluene while the chloroglyoxalate decomposition shows a rate response of only $ca.$ 14 in passing from the solvent tetralin to nitrobenzene.

The most striking result of the present study appears in the relative thermal stabilities of the alkyl chloroglyoxalates when compared with those of the corresponding chlorosulfinates and chloroformates. From consideration of rate data in the literature it is clear that the order of thermal stabilities is chloroglyoxalates > chloroformates > chlorosulfinates. Thus, Wiberg and Shryne[13c] reported a rate constant of 2.11×10^{-3} sec.$^{-1}$ for the first-order decomposition of α-phenethyl chloroformate at 90° in toluene while our value for the chloroglyoxalate IIId is 0.998×10^{-5} sec.$^{-1}$ at 108° in tetralin. From these data, one may estimate a rate difference of roughly 1000-fold for the decomposition of the chloroformate and the chloroglyoxalate, while the α-phenethyl chlorosulfinate is so unstable that it cannot be isolated.[13c] Lewis and Boozer[12a] found a rate constant of 6.16×10^{-3} sec.$^{-1}$ for the decomposition of 2-octyl chlorosulfinate at 98.5° in dioxane and, while quantitative data for 2-octyl chloroformate are not available, it is apparent from early studies that decomposition of this compound (with a preponderance of retention of configuration) does occur rapidly at relatively low temperatures in a variety of solvents.[13a,b] In sharp contrast, only very slight decomposition could be induced in 2-octyl chloroglyoxalate, even when the substance was heated to temperatures of 200–250°. Our original expectation then, that the alkyl chloroglyoxalates should show thermal stability between that of the chlorosulfinates and that of the chloroformates, was not realized.

The observed order of stabilities implies that the activation energy for the decomposition of alkyl chloroglyoxalates is not a simple function of the strength of the alkyl–oxygen bond as has been proposed for the alkyl chlorosulfinate[15c] and chloroformate[13c,15d] decompositions, $i.e.$

$$\text{ROGCl} \xrightarrow{\text{rate determ.}} \text{R}^+ \ ^-\text{OGCl} \qquad \text{(3)}$$

$$\text{G} = \text{SO, CO, COCO}$$

(15) (a) D. J. Cram, $J.\ Am.\ Chem.\ Soc.$, **75**, 332 (1953); (b) S. Winstein and G. C. Robinson, $ibid.$, **80**, 169 (1958); (c) S. H. Sharman, F. F. Caserio, R. F. Nystrom, J. C. Leach and W. G. Young, $ibid.$, **80**, 5965 (1958); (d) K. L. Olivier and W. G. Young, $ibid.$, **81**, 5811 (1959); (e) E. S. Lewis and W. C. Herndon, $ibid.$, **83**, 1955, 1961 (1961).
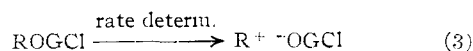
(16) S. G. Smith, A. H. Fainberg and S. Winstein, $ibid.$, **83**, 618 (1961).

(17) J. A. Pegolotti and W. G. Young, $ibid.$, **83**, 3251, 3258 (1961).

(18) (a) S. G. Smith, $ibid.$, **83**, 4285 (1961); (b) A. Gagneux, S. Winstein and W. G. Young, $ibid.$, **82**, 5956 (1960).

If the heterolysis shown in eq. 3 were indeed rate determining for the chloroglyoxalates (G = COCO) as it appears to be for the chlorosulfinates (G = SO) and the chloroformates (G = CO), then, for a given alkyl group, the energy associated with the decomposition would be a simple function of the stability of the anion, $^-$O–G–Cl. From K_a's of related acids,[7] this order of stabilities is clearly $^-$OSOCl > $^-$OCOCOCl > $^-$OCOCl. It follows that some other energy-determining factor is involved in the decomposition of the alkyl chloroglyoxalates; we believe this factor to be the breaking of the *carbon–chlorine bond*.

If cleavage of the carbon–chlorine bond is also involved in the rate-determining step or steps in the decomposition of the alkyl chloroglyoxalates, then the order of reactivities may be rationalized. While the "abnormal positivity" of the dicarbonyl structure in the glyoxalate portion of the molecule should act inductively to facilitate ionization of the alkyl–oxygen bond (relative to that of the chloroformate), by the same token, it would have the effect of strengthening the carbon–chlorine bond, rendering its cleavage more difficult and the over-all reactivity of the alkyl chloroglyoxalates would reflect a balance of two opposing effects.
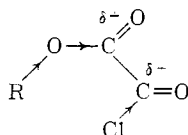
Within the framework of the mechanistic extremes of the SNi reaction discussed earlier (eq. 2), this result could be accommodated either by a somewhat polar version of the cyclic process A in which both the alkyl–oxygen and the carbon–chlorine bonds are directly involved or by a modification of the ionic process B in which the collapse of the ion-pair intermediate is sufficiently slow to contribute to the over-all rate $[i.e., k_{\mathrm{obs}} = k_1 k_2'/(k_{-1} + k_2)]$. In the latter event, however, one would still expect a solvent response characteristic of an ionic process.[19] In view of the rather unimpressive solvent response and consistent with the very large negative entropy of activation which implies a highly specific geometry for the transition state, the chloroglyoxalate decomposition appears to be located in the covalent region of the SNi processes and is better described by the first of the two alternatives given above.

In a recent investigation of the thermal decomposition of thiolsulfonates (RSO$_2$SR) to yield, mainly, thioethers and SO$_2$, Kice and co-workers[20] have brought forth convincing evidence that in these compounds, also, the ease of decomposition is a function not only of the alkyl–sulfur (R–S) bond strength but also of the sulfur–sulfur (S–S) bond strength. As Kice has pointed out,[20b] these reactions bear a strong resemblance to the SNi reactions of chlorosulfinates and chloroformates and it is quite possible that closer scrutiny of the latter reactions will reveal the involvement of more than just the breaking of the R–O bond in those systems as well.

Experimental[21]

Materials.—All alcoholic starting materials were of reagent grade and were carefully purified, dried and distilled before use.

Oxalyl chloride (Eastman Kodak Co., white label) was used without further purification. Anhydrous pyridine was prepared by distillation of the analytical reagent from barium oxide. The solvents used in the kinetic studies were carefully purified, dried and distilled through an 18-inch Vigreux column, a heartcut being retained for the rate measurements. Resolutions of (±)-2-octanol and (±)-α-phenethyl alcohol were accomplished over the brucine salts of the half-phthalates according to standard procedures.[22,23] Authentic samples of (±)-2-chlorooctane, b.p. 169–170° at 584 mm., n^{20}D 1.4270; 2-octene, b.p. 121–122° at 589 mm.; and (±)-α-phenethyl chloride, b.p. 84–85° at 21 mm., n^{25}D 1.5255, were prepared by standard methods for purposes of instrument calibration.

Alkyl Chloroglyoxalates. General Procedure.—To 0.10 mole of oxalyl chloride protected from atmospheric moisture an equimolar amount of the appropriate alcohol was added dropwise with stirring over a period of 30–45 minutes. Evolution of hydrogen chloride accompanied the addition of the alcohol. Stirring was continued at room temperature or slightly higher (35°) for an additional 30 minutes to ensure completion of the reaction. The alkyl chloroglyoxalate was isolated as a middle fraction by direct vacuum distillation of the reaction mixture. Properties and typical yields of the alkyl chloroglyoxalates prepared in this manner are shown in Table V.

TABLE V

ALKYL CHLOROGLYOXALATES

R	B.p. °C.	mm.	n^{20}D	Yield, %	Formula	Chlorine,[a] % Calcd.	Found
C$_2$H$_5$	52–53	37	1.4170	40	C$_4$H$_5$O$_3$Cl	25.89	25.63
n-C$_4$H$_9$	78–80	10	1.4368	60	C$_6$H$_9$O$_3$Cl	21.40	21.20
2-C$_8$H$_{17}$	70–74	0.5	1.4321	65	C$_{10}$H$_{17}$O$_3$Cl	16.07	15.93
CH$_3$CHPh[b]	80–83	0.3	1.5094	59	C$_{10}$H$_9$O$_3$Cl	16.68	16.51

[a] Analysis by potentiometric titration of chloride ion with silver nitrate following hydrolysis of the alkyl chloroglyoxalate. [b] This compound was also prepared from oxalyl chloride and the sodium salt of α-phenethyl alcohol following the procedure of Wiberg and Shryne[13c] for the corresponding chloroformate. For the chloroglyoxalates, the latter method appears to offer no marked advantage over the simpler procedure described here.

Active 2-Octyl Chloroglyoxalates (IIIc).—Both the (+)- and (−)-2-octyl chloroglyoxalates were prepared by the general procedure in yields of 60–70%. The observed rotations (neat, $l = 1$) of the active compounds were of the same sign and close to 2.55 times the observed rotations of the alcohols from which they were prepared. Hydrolysis of active IIIc, achieved by refluxing a sample with 1 N NaOH for 30 minutes, regenerated the starting alcohol with no loss of optical activity.

Active α-Phenethyl Chloroglyoxalates (IIId).—The corresponding active α-phenethyl alcohols were converted to (+)- and (−)-α-phenethyl chloroglyoxalates by the procedure described. The observed rotations (neat, $l = 1$) of the active compounds were consistently very close to 2.40 times the observed rotations of the starting alcohols. Hydrolysis of active IIId yielded the original alcohol with undiminished activity.

Decomposition of Alkyl Chloroglyoxalates in the Presence of Pyridine. Method 1.—One to 0.5 mmole of the chloroglyoxalate was treated with an equimolar quantity of pyridine.[24] The flask was immediately attached to a reflux condenser fitted to a Dry Ice–acetone trap leading to a gas buret filled with saturated sodium chloride solution. A bath of the desired temperature was applied, and the volume of evolved gases was measured (see Table I). When a catalytic amount of pyridine was used, a white solid was observed to sublime and collect in the condenser shortly after the heating period was started. The involuntary removal of this solid caused the reaction to slow down and finally to stop completely. Upon the addition of more pyridine, the reaction started again. A sample of the sublimate was isolated and was found to be very hygroscopic; m.p. 138–140°. The substance gave a positive test for chloride ion but no evidence for oxalate or carbonate ion. The sample, when treated with picric acid, gave pyridine picrate, m.p. 163–165° (reported[25]

(19) We are indebted to referee I for this point: "... for the magnitude of k_2 to exert any sizable effect on the over-all rate, $k_2 \ll k_{-1}$; but in that event, $k_{\mathrm{obs}} = k_1 k_2/k_{-1}$. While k_2 will certainly vary with solvent in a manner exactly opposite to k_1, k_{-1} will also decrease with increasing solvent ionizing power in a manner that will probably come close to compensating for much of the variation in k_2. In other words, the ratio k_2/k_{-1} will not be strongly sensitive to solvent and any effect of solvent on rate will be the result of its effect on k_1."

(20) (a) J. L. Kice, F. M. Parham and R. M. Simons, *J. Am. Chem. Soc.*, **82**, 834 (1960); (b) J. L. Kice and F. M. Parham, *ibid.*, **82**, 6168 (1960).

(21) Optical rotations were measured with an Adam Hilger Ltd. polarimeter in a water-jacketed semimicro polarimeter tube. Density and rotatory constants used in the calculations of specific rotations and optical purities were: 2-octanol, d^{25}₄ 0.819, $[\alpha]^{25}$D ±9.74° (from $[\alpha]^{25}$D ±9.9° and Δα/Δt)[8]; 2-chlorooctane, d^{25}₄ 0.861, $[\alpha]^{25}$D ±36.1°[9]; α-phenethyl alcohol, d^{25}₄ 1.01, $[\alpha]^{22}$D ±43.4°[8,10]; α-phenethyl chloride, d^{25}₄ 1.06, $[\alpha]^{25}$D (min.) ±103.6°,[11] $[\alpha]^{25}$D (max.) ±119°[11]; styrene, d^{25}₄ 0.908.

(22) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1951, p. 489.

(23) E. Downer and J. Kenyon, *J. Chem. Soc.*, 1156 (1939).

(24) Upon the addition of the pyridine to the chloroglyoxalate, a white fluffy solid formed in the reaction vessel. This solid, which is presumed to be the pyridinium salt of the chloroglyoxalate, slowly disappeared during the course of the reaction.

m.p. 167°). The white solid appears to be pyridine hydrochloride, reported to melt at 144°.[26]

Method 2.—To a flask equipped with a nitrogen inlet tube was added 10 to 15 mmoles of the chloroglyoxalate and an equimolar quantity of pyridine. The flask was fitted to a reflux condenser leading to an absorption tube filled with Ascarite. A bath was then applied, and the system was flushed with a slow stream of nitrogen during the reaction. The amount of carbon dioxide evolved was determined from the increase in weight of the absorption tube.

The same general procedures were used in the preparative runs, except that 20–25 mmoles of the chloroglyoxalate was used and no attempt was made to measure the evolved gases.

Product Isolation from the Pyridine-induced Decompositions. —Ethyl chloride, formed in the decomposition of ethyl chloroglyoxalate, was isolated from the Dry Ice–acetone trap and identified by g.l.p.c. by comparison of its fractogram with that of an authentic sample. The products of the decomposition of *n*-butyl and 2-octyl chloroglyoxalate were isolated by dissolving the reaction mixture in 25 ml. of ether and washing the ethereal extract successively with cold, 10-ml. portions of water, 1 *N* hydrochloric acid, 5% sodium carbonate solution and, finally, water. Distillation of the dried extracts afforded the corresponding chlorides: *n*-butyl chloride, b.p. 63–65° at 591 mm., $n^{20}D$ 1.4010; 2-chlorooctane (plus 2-octene), b.p. 159–160° at 590 mm., $n^{20}D$ 1.4260.

Direct distillation of the reaction mixture from the decomposition of α-phenethyl chloroglyoxalate yielded α-phenethyl chloride (plus styrene), b.p. 85–87° at 25 mm., $n^{25}D$ 1.5243.

Decomposition of α-Phenethyl Chloroglyoxalate in the Presence of Solvent.—The same method was employed to measure the total gases evolved as in the decomposition in the absence of solvent except that the solvent (10 to 15 ml.) was equilibrated with the bath before the reactants were added; g.l.p.c. analyses were performed directly on the reaction mixtures. Attempts at product isolation were made only for the decompositions carried out in nitrobenzene and in carbon tetrachloride. The procedures followed were those outlined below for the active compound.

Product Analyses.—The compositions of the product mixtures obtained in the decompositions of the alkyl chloroglyoxalates were determined by g.l.p.c. in a Perkin–Elmer Corp. model 154C vapor fractometer equipped with a Leeds and Northrup recorder with a 1-millivolt full-scale deflection. In the identification of ethyl and *n*-butyl chlorides, produced from the corresponding chloroglyoxalates, a Perkin–Elmer "A" column (2 m., 0.25 inch diameter, with diisodecyl phthalate substrate on Celite) was used with cabinet temperatures of 37 and 70°, respectively, and a helium flow rate of 60 ml./min. For the analyses of the product mixtures from the decomposition of 2-octyl and α-phenethyl chloroglyoxalates, a 2-m., 0.25 inch diameter column with a 0.125% Reoplex-400 substrate on 60–80 mesh micro glass beads (Micro Beads, Inc., Toledo, Ohio) was used. Analyses were carried out at cabinet temperatures of 60–75°, helium flow rates of 60 ml./min., and with a heated injection block to assure rapid vaporization of the samples. Prior to each analysis, the column was calibrated with standard mixtures of the components.

Decomposition of Active 2-Octyl Chloroglyoxalate in the Presence of Pyridine.—According to the procedure outlined for the racemic compound, 5.51 g. (0.025 mole) of (−)-2-octyl chloroglyoxalate, prepared from (−)-2-octanol, $[\alpha]^{25}D$ − 9.54° (neat), was decomposed in the presence of 1.98 g. (0.025 mole) of pyridine by heating at 100° for 6 hours. The resulting 2-chlorooctane, isolated by the previously described procedure, showed $\alpha^{25}D$ +23.83° (neat, l = 1) and consisted of 84.6% by weight of chloride and 15.4% by weight olefin and residual solvent. Corrected for olefin content, the specific rotation of the 2-chlorooctane is $[\alpha]^{25}D$ +33.7° (neat), corresponding to 95.4% inversion.[27]

Decomposition of Active α-Phenethyl Chloroglyoxalate in the Presence of Pyridine.—To 50 ml. of carbon tetrachloride were added 2.37 g. (0.03 mole) of pyridine and 6.80 g. (0.032 mole) of (−)-α-phenethyl chloroglyoxalate, prepared from (−)-α-phenethyl alcohol, $[\alpha]^{25}D$ − 22.70°. The solution, protected from atmosphere moisture, was heated at reflux for 10 hours. After removal of 35–40 ml. of the solvent by distillation at atmospheric pressure, the remaining solution, decanted from a small amount of tan, gummy residue, was fractionally distilled at 18 mm. to yield 2.30 g. (51%) of α-phenethyl chloride, b.p.

76–78°, $[\alpha]^{25}D$ +53.4° (neat). The latter rotation corresponds to 85.8% (min.) to 98.5% (max.) inversion.

Attempted Thermal Decomposition of 2-Octyl Chloroglyoxalate. —Samples of 2-octyl chloroglyoxalate were heated both neat and in various solvents to temperatures up to 240° with little or no decomposition occurring. The 2-octyl chloroglyoxalate, when dripped onto crushed Pyrex glass heated to 240°, distilled at 215–218° at 590 mm. with only a small percentage (5%) of decomposition occurring.

Thermal Decomposition of Active α-Phenethyl Chloroglyoxalate in the Absence of Solvent.—(−)-α-Phenethyl chloroglyoxalate (3.00 g.) prepared from (−)-α-phenethyl alcohol, $[\alpha]^{25}D$ − 16.60°, was heated under a pressure of 39 mm. for 36 hours in a bath maintained at 125°. Under these conditions, the α-phenethyl chloride distilled from the reaction zone almost as soon as it formed. The distillate (0.51 g.) was found to contain 60% α-phenethyl chloride and 40% styrene by weight, $[\alpha]^{25}D$ − 2.17°. A correction for olefin content gives $[\alpha]^{25}D$ − 3.62° for the α-phenethyl chloride, a rotation which corresponds to 90.9% (min.) − 92.1% (max.) racemization.

Thermal Decomposition of Active α-Phenethyl Chloroglyoxalate in Nitrobenzene.—(−)-α-Phenethyl chloroglyoxalate (2.50 g.), prepared from (−)-α-phenethyl alcohol, $[\alpha]^{25}D$ − 16.60°, was heated in 35 ml. of nitrobenzene for 14 hours at 108°. At the end of the heating period the reaction mixture was directly distilled at 12 mm. to give 1.07 g. of a light yellow first fraction b.p. 35–80°; g.l.p.c. analysis of this fraction showed that it contained 0.28 g. of α-phenethyl chloride per milliliter of solution. The remainder of the fraction was nitrobenzene. A 1-dm. length of this same solution showed $\alpha^{25}D$ − 4.60° or $[\alpha]^{25}D$ − 16.45° (nitrobenzene, c 28), corresponding to 57.0% (min.) to 65.4% (max.) retention of configuration.

Rotation of Active α-Phenethyl Chloride in Nitrobenzene.[28]— A sample of (+)-α-phenethyl chloride, $[\alpha]^{25}D$ +33.80° (neat) dissolved in purified nitrobenzene (c = 28 g./100 ml.) gave $\alpha^{25}D$ +6.00° (l = 1), which corresponds to $[\alpha]^{25}D$ +21.43° (nitrobenzene, c 28). From this observation and Hart's values for the homogeneous chloride[11] the following limits were calculated for the specific rotation of optically pure α-phenethyl chloride in nitrobenzene solution: $[\alpha]^{25}D$ (max.) ±75.4° (nitrobenzene, c 28), $[\alpha]^{25}D$ (min.) ±65.7° (nitrobenzene, c 28).

Thermal and HCl-induced Racemization of Active α-Phenethyl Chloride.[28]—Purified nitrobenzene saturated with hydrogen chloride (dried by passage through concd. H_2SO_4) at room temperature was held at 108° for 1 hour to produce a saturated solution of hydrogen chloride in nitrobenzene at that temperature. The HCl content of the solution was determined by extracting an aliquot with water and titrating the liberated acid with standard base. The solution, saturated at 108°, was found to be 0.12 *N* in HCl. Dilution of the saturated solution with purified nitrobenzene produced the 0.05 *N* solution used below.

To determine the maximum amount of racemization attributable to the presence of hydrogen chloride in the decomposition in nitrobenzene, a solution 0.36 *M* in (+)-α-phenethyl chloride and 0.12 *N* in HCl was prepared, $\alpha^{25}D$ +0.87° (l = 1). After 10 hours at 108°, the observed rotation had fallen to $\alpha^{25}D$ + 0.44° (l = 1), a result which corresponds to 49.5% racemization. The minimum amount of racemization attributable to the HCl-induced process was determined in a parallel experiment using a solution 0.36 *M* in (+)-α-phenethyl chloride and 0.05 *N* in HCl (corresponding to the styrene content of the product). After 10 hours at 108° the observed rotation of the solution had changed from $\alpha^{25}D$ +1.22° (l = 1) to $\alpha^{25}D$ +1.10° (l = 1), a total racemization of 9.84%.

Determination of Thermal Stability of α-Phenethyl Chloride. A.—A sample of α-phenethyl chloride, protected from atmospheric moisture, was heated neat for 16 hr. at 108°; g.l.p.c. analysis of the light tan product showed less than 0.1% free styrene in the chloride. By comparison with a sample of pure α-phenethyl chloride it appeared that about 5% of the original chloride had been diverted to high boiling material by the thermal treatment.

B.—Gas–liquid partition chromatographic analysis of a solution of 0.32 g. of α-phenethyl chloride in 10 ml. of nitrobenzene which had been held at 108° for 16 hours revealed the presence of less than 1% styrene as the only impurity. No polymeric material could be detected.

Rate Studies.—The apparatus used has been described in detail by Schubert[29] and Wiberg and Shryne.[13e] In essence, it consisted of a glass reaction flask attached to a water-jacketed gas measuring buret filled with saturated salt solution and adapted for continuous volume readings at atmospheric pressure. The connections between the reaction flask and the gas measuring system were of flexible rubber tubing to permit agitation of the reaction mixture by mechanical shaking of the flask. The reaction flask, immersed in a thermostated oil-bath, was shaken through an arc of about 4 inches at the rate of 100 swings per

(25) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 296.

(26) L. F. Audrieth, A. Long and R. E. Edwards, *J. Am. Chem. Soc.*, **58**, 428 (1936).

(27) Sample calculation for product mixture containing 84.6% by weight of 2-chlorooctane, 14.7% by weight of 2-octene and 0.7% of solvent ether, $\alpha^{25}D$ obsd. +23.83°, d^{25}_4 0.835: $[\alpha]^{25}D$ for 2-chlorooctane = +23.83/(0.846 × 0.835) = +33.7°; % inversion = (33.7 × 9.74 × 100)/(36.1 × 9.54) = 95.4%.

(28) We are indebted to Mr. Richard W. Hasbrouck for these experiments.

(29) W. M. Schubert, *J. Am. Chem. Soc.*, **71**, 2639 (1949).

minute. To start a run, 10 ml. of the solvent was introduced into the reaction vessel and allowed to equilibrate. The shaking was momentarily interrupted while a sample of α-phenethyl chloroglyoxalate (1.9–3.1 mmoles) was introduced by means of a hypodermic syringe through a serum bottle stopper on the side-arm of the flask. Shaking was resumed and the volume of the evolved gases was read at various intervals. The bath temperature was maintained within ±0.1°. The buret jacket temperature was 20.00 ± 0.05°.

First-order rate constants were evaluated from plots of log $(V_\infty - V)$ against time.[30] Straight lines were obtained up to 80% reaction in some of the faster runs. In all the runs, 0.5–1.5 g. of powdered Pyrex glass was added to the reaction vessel in order to prevent supersaturation of the solvent by the evolved carbon monoxide and carbon dioxide. The powdered glass had no effect on the rate constants. After each run the reaction flask and the powdered glass were cleaned thoroughly by rinsing with acetone followed by water. The flask was then soaked in chromic acid solution and finally in distilled water. The water was removed by flaming. The rate constants so obtained are presented in Table IV. Data for typical runs are reproduced in Table VI.

From a plot of log k vs. $1/T$ the rate data for the decompositions in nitrobenzene were fitted to the Arrhenius equation. From the experimental E_{act} obtained (19.8 kcal./mole) an activation enthalpy of 19.0 kcal./mole and entropy of activation of −27 e.u. were calculated for $T = 381.4°$K. from the relationships $\Delta H^{\ddagger} = E_{act} - RT$ and $\Delta S^{\ddagger} = R \ln k - R \ln (k'T/h) + \Delta H^{\ddagger}/T$. Uncertainties in E_{act} and $\Delta H^{\ddagger}$ are estimated at ±1 kcal./mole and, in $\Delta S^{\ddagger}$, at ±2 e.u.

(30) V_∞ was calculated from the weight of the chloroglyoxalate introduced into the reaction vessel. In some of the faster runs, V_∞ was determined experimentally and agreed quite well with the calculated value.

TABLE VI

SAMPLE RATE DATA FOR THE DECOMPOSITION OF α-PHENETHYL CHLOROGLYOXALATE IN NITROBENZENE AT 108.3°

$k = 1.39 \times 10^{-4}$ sec.$^{-1}$, init. concn. of chloroglyoxalate, 2.06 mmoles			$k = 1.36 \times 10^{-4}$ sec.$^{-1}$, init. concn. of chloroglyoxalate, 3.11 mmoles		
t, min.	$(V_\infty - V)$	log $(V_\infty - V)$	t, min.	$(V_\infty - V)$	log $(V_\infty - V)$
0	127.8	2.107	0	195.2	2.290
12	119.6	2.077	6	188.5	2.275
24	109.1	2.038	12	180.6	2.257
36	99.3	1.997	18	172.1	2.236
48	89.6	1.952	24	163.8	2.214
60	80.6	1.906	30	155.6	2.192
72	72.6	1.861	36	148.8	2.172
84	65.4	1.816	42	140.2	2.147
96	59.1	1.771	48	132.8	2.123
108	53.6	1.729	54	126.1	2.101
120	48.7	1.688	60	119.7	2.079
132	44.1	1.644	66	113.5	2.055
144	40.2	1.604	72	107.6	2.028
156	36.7	1.564	78	102.4	2.011

Stability of Cumylperoxy Radical–Pyridine Charge-Transfer Complex

BY J. R. THOMAS

In oxidizing cumene the steady-state cumylperoxy radical concentration can be determined by electron spin resonance. In the presence of pyridine, a strong donor molecule for charge-transfer complex formation, the total free-spin concentration should be increased by the term $[RO_2\cdot]_{s.s.}$[pyridine]K, where K is the equilibrium constant for complex formation $RO_2\cdot$ + pyridine $\rightleftarrows$ $[RO_2^{-}\cdots^{+}$pyridine]. At 57 and 40° no increased free-spin concentration is observed in 1 M pyridine solutions. It is concluded that K must be less than 0.4 l./mole. Measurement of the time required to reach steady-state cumene oxidation at 57° in the presence of pyridine leads to a similar conclusion.

Porter and Smith[1] have explained the influence of chaperon molecules upon the recombination rate of iodine atoms in terms of a charge-transfer complex intermediate between the two species. With such materials as ethyl bromide and benzene, Grover and Porter[2] and Strong, et al.,[3,4] have observed transient optical absorption bands which have been shown to be due to this type of iodine atom complex. Russell[5] has shown that pronounced solvent effects upon chlorination reactions can be explained in terms of chlorine-atom substrate complexes of similar nature. As a result of kinetic studies of hydrocarbon oxidation inhibition by aromatic amines and phenols, Boozer and Hammond[6,7] have postulated the rapid, reversible formation of charge-transfer complexes between such inhibitors and alkylperoxy radicals as the critical step in the inhibition mechanism. Recent studies in this field[8] have confirmed the kinetic results of these investigators which, to date, can only be reasonably explained in terms of such complex species.

This paper reports studies of cumene oxidation by electron spin resonance and kinetic techniques leading

(1) G. Porter and J. A. Smith, Proc. Roy. Soc. (London), A261, 28 (1961).

(2) T. A. Grover and G. Porter, ibid., A262, 476 (1961).

(3) S. J. Rand and R. L. Strong, J. Am. Chem. Soc., 82, 5 (1960).

(4) R. L. Strong, S. J. Rand and J. A. Britt, ibid., 82, 5053 (1960).

(5) G. A. Russell, ibid., 80, 4987 (1958).

(6) C. E. Boozer and G. S. Hammond, ibid., 76, 3861 (1954).

(7) C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, ibid., 77, 3233 (1955).

(8) J. R. Thomas and C. A. Tolman, ibid., 84, 2930 (1962).

to the conclusion that the equilibrium constant for complex formation between cumylperoxy radical and pyridine is small.

Experimental

Materials.—Cumene was Eastman white label passed through a silica column. Benzene and pyridine were J. T. Baker research grade. Azobisisobutyronitrile was recrystallized from methanol.

Electron Spin Resonance Studies.—A Varian Model 4500 spectrometer with 100 kc. modulation was used. The oxidation reactor was a 5-liter flask equipped with a bubbler for saturating the solution with oxygen. The reactor was located immediately above the microwave cavity. Solution was flowed through the cavity via a quartz tube. At flow rates of the order of 1 l./min. the intensity of the resonance was independent of rate. At 0.2 l./min. the intensity was reduced. When flow through the cavity was stopped, the resonance disappeared completely in several minutes.

The experimental arrangement was calibrated with diphenyl nitric oxide solutions of known concentration. Radical concentrations were determined by double integration of the derivative line. Reproducibility was ±20% for identical experiments. The absolute radical concentrations are estimated to be within ±50%.

Oxidation Studies.—The oxidator was a stirred reactor in conjunction with a sensitive gasometer. The reactor, which served also as the gas reservoir, was completely immersed in a regulated water bath. In all cases the system was brought to thermal equilibrium without initiator. At time zero a small volume of prewarmed initiator solution was injected into the system throughout a controlled opening. Carefully done, this caused very slight upset to the system.

Results and Discussion

At low temperatures the oxidation of cumene by molecular oxygen is a simple chain reaction. When