[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF ATLANTA UNIVERSITY AND MOREHOUSE COLLEGE]

THERMAL DECOMPOSITION OF DIALKYL PEROXYDICARBONATES IN SOLUTION: REACTIONS OF ALKOXY FREE RADICALS IN PURE[1] SOLVENTS

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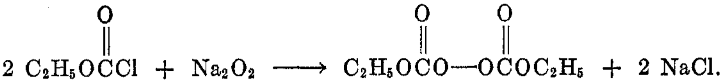
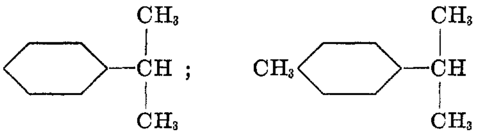
In 1925 Wieland (1) reported the preparation of diethyl peroxydicarbonate by the following method:



$$2\ C_2H_5O\overset{O}{\overset{\|}{C}}Cl + Na_2O_2 \longrightarrow C_2H_5O\overset{O}{\overset{\|}{C}}O{-}O\overset{O}{\overset{\|}{C}}OC_2H_5 + 2\ NaCl.$$

In a more recent paper Strain (2) and his co-workers have reported the synthesis of an extensive series of these esters of peroxydicarbonic acid using the same method for their preparation. These latter workers have studied the kinetics of the thermal decomposition reactions of these peroxides in the gas phase and in solution and have reported these reactions to be essentially of first order with respect to the peroxide concentration and to have velocities which are nearly independent of the nature of the solvent. Still more recently Cohen and Sparrow (3) have studied the thermal decomposition of diisopropyl peroxydicarbonate in several solvents including ethylbenzene. They report the reactions to be principally of first order and to have rates which are independent of the nature of the solvent. In the reaction with ethylbenzene these workers (3) have used small quantities (0.018 mole) of peroxide and have thus failed to isolate one of the reaction products (acetone) whose appearance is pertinent to the proper interpretation of the course of the reactions. Unaware, at the outset, of the then unreported works of these researchers, we had set out to study the thermal decomposition reactions of same group of compounds. All the reactions here reported have been carried out in solution of some relatively high-boiling solvent using quantities of the peroxides ranging from 0.1 mole to 1.2 moles. In this work the interest has been centered not upon the kinetics of these decompositions, but upon the fate of the supposed free radical intermediates as suggested by the nature and the quantities of the various reaction products therefrom obtained.

Throughout this work two types of solvents have been used: *Type A:* Solvents having at least one hydrogen which succumbs quite readily to abstraction by alkyl free radicals in solution, *e.g.*, Cumene, *p*-cymene:



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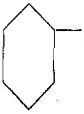
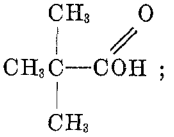
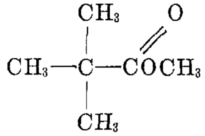
[1] A later publication will report reactions of alkoxy free radicals in mixed solvents.

[2] Taken from a master's thesis submitted to the department of chemistry, Atlanta University, 1950.

Type B: Solvents having all primary hydrogens (not adjacent to activating groups such as —, COOH, COOR, CN, COR, etc.) which succumb only with great difficulty to abstraction by alkyl free radicals in solution; *e.g.*, trimethylacetic acid, methyl trimethylacetate:



$\mathrm{CH_3}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\text{—}\overset{\mathrm{O}}{\mathrm{C}}\mathrm{OH}$;



$\mathrm{CH_3}\text{—}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\text{—}\overset{\mathrm{O}}{\mathrm{C}}\mathrm{OCH_3}$

This classification of these solvents is based upon previous work using purely alkyl free radicals as hydrogen abstractors (4).

This paper is a report of the course of the reactions of several alkoxy free radicals, RO•, when generated in presence of each of these two types of solvent molecules. It reports the tendency of a given alkoxy free radical to abstract an hydrogen atom from the solvent molecule and/or from the parent substance, the dialkyl peroxydicarbonate itself. (This latter course of reaction is termed disproportionation, see below.) Here also are included some data for comparing the reactions involving the abstraction of hydrogen from solvent and the disproportionation reactions of alkoxy free radicals with the same reactions of some alkyl free radicals. All these data appear in tabulated form in Table I and Table II.

The factors believed to make significant contributions to the activation energies of displacement reactions have been well established (5). The outline below shows how these free radical displacement reactions (reactions involving abstraction of hydrogen atoms from solvent molecule) as well as the subsequent dimerizations of the residual free radicals might be interpreted in this light.

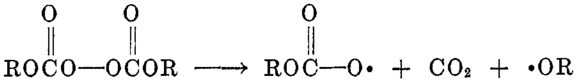
1. The Energy Factor
   - A. The relative reactivities of the alkoxy free radicals toward hydrogen abstraction.
   - B. The relative tendencies of alkoxy free radicals to decompose to give a carbonyl compound and an alkyl free radical.
   - C. The relative strengths of the bonds holding the univalent atoms in the solvent molecules.
2. The Repulsion Factor
   - A. The repulsion between substituents in the solvent molecule and the approaching alkoxy free radical.
   - B. Repulsion between dimerizing residual free radicals of first order:[3] the orientation effect.

[3] "Initial free radicals" are formed through homolytic fission which is either thermally or photolytically induced. The initial free radical/s reacts with a solvent molecule to extract an hydrogen atom therefrom. The solvent molecule is thus converted into a "residual free radical of first order." In selected cases this residual free radical of first order might react with solvent by radical exchange to produce an isomeric free radical

3. The Steric Factor
   A. The steric effect during hydrogen abstraction.
   B. The steric effect in the dimerizing residual free radicals of first order.[3]

The evidence presented in this paper deals largely with factor 1, the energy factor. The possible significance of factor 2, the repulsion factor, will be treated in a forthcoming publication.

The following reaction scheme for the generation of these alkoxy free radicals by thermal decompositions of the peroxides is consistent with the experimental facts.



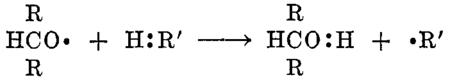
$$\mathrm{RO}\overset{\overset{\textstyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{O{-}O}\overset{\overset{\textstyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OR} \longrightarrow \mathrm{RO}\overset{\overset{\textstyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}O}\cdot + \mathrm{CO_2} + \cdot\mathrm{OR}$$

These alkoxy free radicals, •OR, might dimerize to form dialkyl derivatives of hydrogen peroxide, but this dimerization is forbidden at the temperature of these experiments. Three other possible courses are as follows:

I. Decomposition to an alkyl free radical and a carbonyl compound (6).

$$\mathrm{(CH_3)_3C{-}O}\cdot \longrightarrow \cdot\mathrm{CH_3} + \mathrm{(CH_3)_2C{=}O}$$

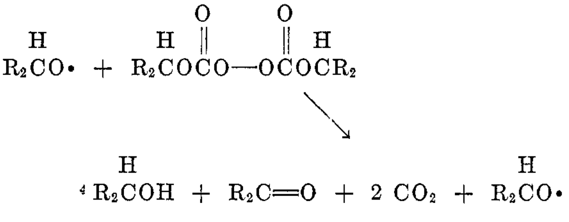
II. Abstraction of an hydrogen atom from the solvent molecule with subsequent dimerization of the residual free radical obtained from the solvent molecule (9).



$$\mathrm{H}\underset{\mathrm{R}}{\overset{\mathrm{R}}{\mathrm{C}}}\mathrm{O}\cdot + \mathrm{H{:}R'} \longrightarrow \mathrm{H}\underset{\mathrm{R}}{\overset{\mathrm{R}}{\mathrm{C}}}\mathrm{O{:}H} + \cdot\mathrm{R'}$$

$$\cdot\mathrm{R'} + \cdot\mathrm{R'} \longrightarrow \mathrm{R'{:}R'}$$

III. Abstraction of hydrogen from the parent peroxide; disproportionation (2).



$$\mathrm{R_2}\overset{\mathrm{H}}{\mathrm{C}}\mathrm{O}\cdot + \mathrm{R_2}\overset{\mathrm{H}}{\mathrm{C}}\mathrm{O}\overset{\overset{\textstyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{O{-}O}\overset{\overset{\textstyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{O}\overset{\mathrm{H}}{\mathrm{C}}\mathrm{R_2} \searrow {}^{4}\,\mathrm{R_2}\overset{\mathrm{H}}{\mathrm{C}}\mathrm{OH} + \mathrm{R_2C{=}O} + 2\,\mathrm{CO_2} + \mathrm{R_2}\overset{\mathrm{H}}{\mathrm{C}}\mathrm{O}\cdot$$

No evidence for the occurrence of the direct decomposition reaction (scheme I) was disclosed in our studies. Rust, Suebold, and Vaughan (6) have reported that a series of low molecular weight alkoxy free radicals when generated in a solution of cyclohexene undergo essentially two types of reactions, namely: decomposition to an alkyl radical and a ketone, and abstraction of an hydrogen

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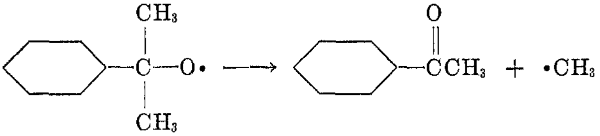
which we call a residual free radical of second order, etc. Direct evidence of such phenomenon will appear in a forthcoming publication.

[4] One product here is a primary or secondary alcohol while the other is an aldehyde or ketone, depending on the nature of the R's in the alkoxy free radical, $\mathrm{R_2CHO}\cdot$.

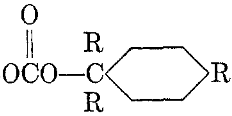
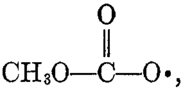
atom from the solvent molecule to form an alcohol. Their decomposition reactions have been carried out in gas phase at 195°. The mean free time of such a particle in gas phase is of the order of 10^{-10} seconds, while in the liquid phase the mean free time is reduced to 10^{-13} seconds (7). Such a difference in mean free time in the two states, gaseous and liquid, together with the difference in temperature of the two sets of experiments (130° ± *vs.* 195°) is here proposed as a possible explanation for the absence of reaction scheme I in our experiments. It is very probable that in the liquid phase the alkoxy radical attacks either the solvent molecule or the parent peroxide molecule before there is time for the necessary redistribution of energy within the radical itself if it is to break up into ketone and alkyl free radical. This redistribution of energy giving rise to the ketone-producing reaction (scheme I) is possibly favored at the higher temperature. In support of this postulate there was observed in the work here reported evidence for only two types of reactions on the part of the alkoxy free radicals: reactions according to scheme II and scheme III.

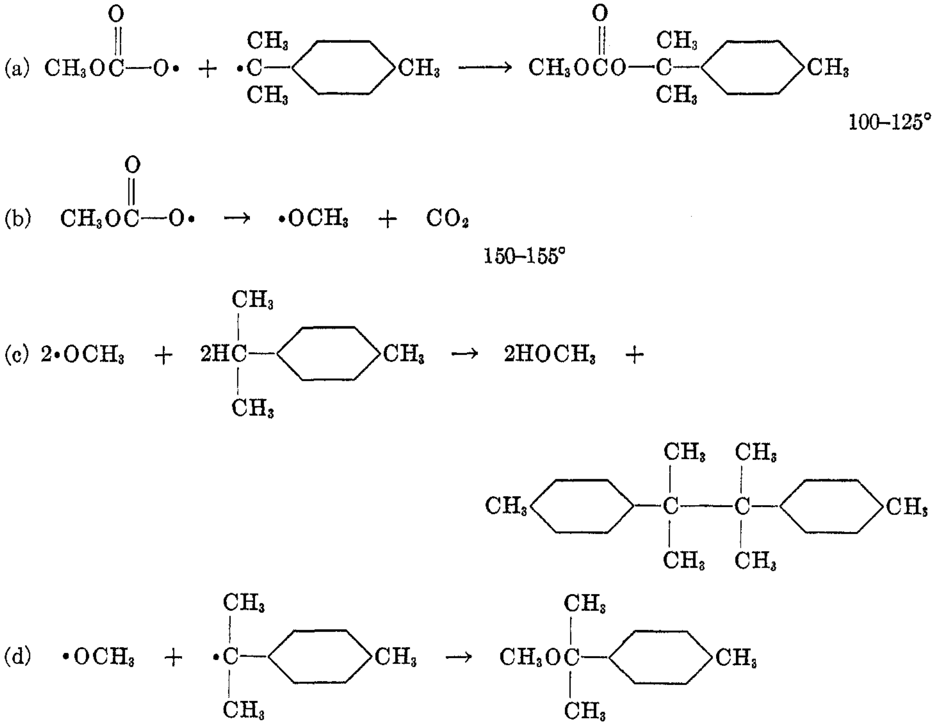
Note, however, that Kharasch and co-workers (8) have reported this type (scheme I) of direct decomposition of *aralkoxy* free radicals even in solution at the lower temperatures (130–140°)



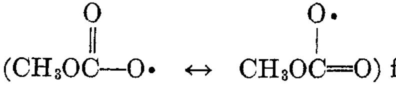
This suggests that these *aralkoxy* free radicals of the type included in the Kharasch studies are inherently less effective than purely *alkoxy* free radicals at abstracting hydrogen atoms from neighboring molecules and hence have longer half-life periods in solution. This gives rise to greater opportunity for the direct decomposition type of reaction (scheme I). It is well known that the *tert*-butoxy free radical undergoes this direct decomposition reaction (scheme I) in solution at the lower temperature (9a, b, c, d). Here again, this *tert*-butoxy free radical reacts to abstract an hydrogen atom from the solvent (scheme II) when the solvent molecule yields its H atom/s very readily. When generated under conditions which increase the half-life period, *i.e.*, in gas phase or in solvents which have all difficultly abstractable hydrogens, this *tert*-butoxy free radical then undergoes direct decomposition (scheme I) to a greater extent (9, 10).

Our study includes only low molecular weight alkoxy free radicals (methoxy to *n*-butoxy), and in all cases studied the reaction scheme II predominated when the solvent molecule, H:R′, was isopropylbenzene or *p*-cymene, (Type A). When the solvent molecule, H:R′, was trimethylacetic acid, or methyl trimethylacetate, (Type B), the reaction scheme III occurred to a greater extent using the same alkoxy free radical. In some cases scheme II almost completely disappeared as the solvent molecule was changed from type A to type B using the same alkoxy free radical.

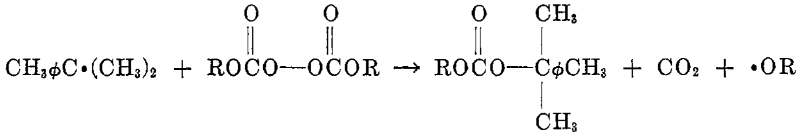
Although there is here no conclusive proof, the evidence strongly suggests that there are alkyl aralkyl carbonate esters formed (alkyl-R) during the decomposition of these peroxides in the type A (cumene, *p*-cymene) solvents. A possible source of such esters is indicated by equation (a) below. Esters of this type are obtained in good yield (see Table I) when these reactions are carried out in cumene or *p*-cymene at temperatures of 100–125°, while the same experiments at higher temperatures, 150–155°, gives rise to lower yields of such esters. Higher yields of alcohol and carbon dioxide are obtained at the higher temperatures. This suggests that the free radical, $CH_3O{-}\overset{\overset{O}{\|}}{C}{-}O\cdot$, exhibits a very distinct thermal coefficient of instability; equation (b) below.



$$(b)\quad CH_3O\overset{\overset{O}{\|}}{C}{-}O\cdot \rightarrow \cdot OCH_3 + CO_2$$

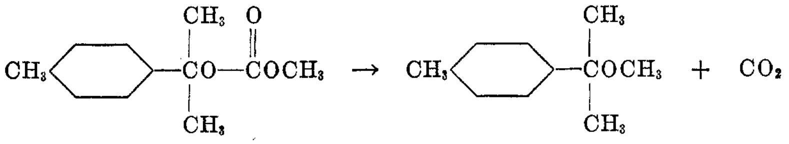
On formal grounds alone one might expect ethers to be formed as products of reaction (d). The fact is they are not. These ethers have appeared only as products of the subsequent destructive distillation (see below) of the esters. Note that the $(CH_3O\overset{\overset{O}{\|}}{C}{-}O\cdot \leftrightarrow CH_3O\overset{\overset{O\cdot}{|}}{C}{=}O)$ free radical is stabilized through resonance. It might survive numerous collisions with solvent molecules without abstracting an hydrogen until it encounters the aralkyl free radical, likewise stable, with which it dimerizes [reaction (a)]. The highly reactive $\cdot OCH_3$ free radical would not survive as many collisions with solvent molecules before it abstracted an hydrogen therefrom [equation (c)]. Reaction (d) is therefore forbidden in these solvents and no ethers are formed.

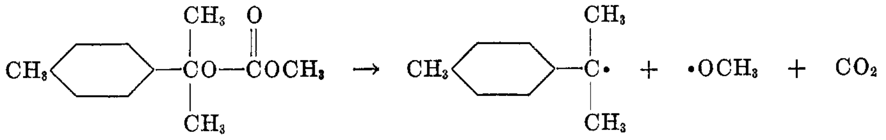
One referee has suggested the following mechanism for the formation of these esters:

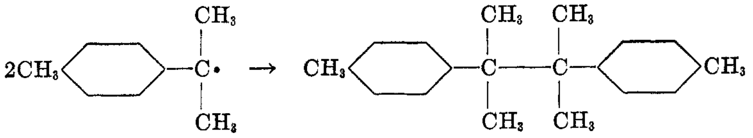
(a′) 

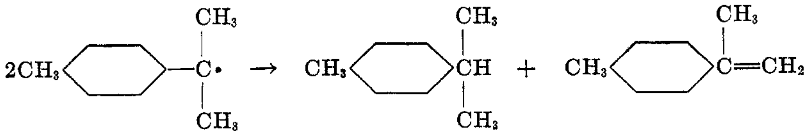
$$CH_3\phi C\cdot(CH_3)_2 + RO\overset{O}{\overset{\|}{C}}O\text{—}O\overset{O}{\overset{\|}{C}}OR \rightarrow RO\overset{O}{\overset{\|}{C}}O\text{—}\underset{CH_3}{\overset{CH_3}{C}}\phi CH_3 + CO_2 + \cdot OR$$

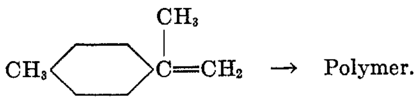
The evidence does not enable one to distinguish between these mechanism, (a) and (a′), for ester formation. They might indeed both be operating in these reactions. These esters are stable at temperatures used to remove the bulk of the unreacted solvents, *p*-cymene and cumene (65°/38 mm. for cumene; 64°/16 mm. for *p*-cymene). The crystalline dimers (2,3-dimethyl-2,3-diphenylbutane and 2,3-dimethyl-2,3-di-*p*-tolylbutane) have been separated from the oily esters by suction filtering. Most of these esters seem to undergo the following type of decomposition when attempts were made to distill them at 0.5 mm. to 1.0 mm. pressure:











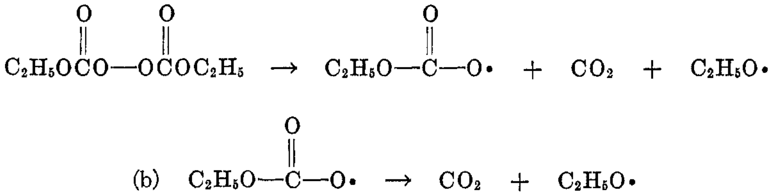
These esters give carbon dioxide and the alkyl alcohol upon hydrolysis. The pure α,α-dimethylbenzyl alcohol or *p*-methyl-α,α-dimethylbenzyl alcohol has not been isolated from the fragments of hydrolysis.[5] The esters lose carbon dioxide and show an increase in carbon content upon repeated distillation until the analyses and molecular weights check with the theoretical values for the corresponding ether. They deposit more of the dimer, dicumene or di-*p*-cymene, upon repeated distillation. They have not been isolated in a state uncontaminated with either the crystalline dimer of the derived ether.

The collected data summarized below in Table I and Table II indicate that under similar conditions of temperature and when reacted with a constant solvent molecule, these various alkoxy free radicals fall in the following approximate order of their decreasing tendencies to react by H-abstraction from the solvent.

$$\cdot OCH_3 > \quad \cdot OC_2H_5 > \quad \begin{matrix} \cdot OC_3H_7(n) \\ \cdot OC_3H_7(\text{iso}) \end{matrix} > \begin{matrix} \cdot OC_4H_9(n) \\ \cdot OC_4H_9(\text{iso}) \end{matrix}$$

Their relative tendencies to react under similar conditions by disproportionation follow the reverse order. The tendency toward formation of the carbonate esters in these reactions is a function of the temperature and of the nature of the solvent molecule. The thermal stability of the carbonate free radical, $RO\overset{\overset{O}{\|}}{C}—O\cdot$, is also an important factor in ester formation. Of the cases here reported the methyl derivative, $(CH_3O\overset{\overset{O}{\|}}{C}—O\cdot)_2$, seems to be the peroxide most effective at ester formation, while *p*-cymene is the solvent from which greatest yields of esters were obtained.

The following over-all reaction scheme is proposed for these reactions:



$$C_2H_5O\overset{\overset{O}{\|}}{C}O—O\overset{\overset{O}{\|}}{C}OC_2H_5 \rightarrow C_2H_5O—\overset{\overset{O}{\|}}{C}—O\cdot + CO_2 + C_2H_5O\cdot$$

$$\text{(b)} \quad C_2H_5O—\overset{\overset{O}{\|}}{C}—O\cdot \rightarrow CO_2 + C_2H_5O\cdot$$

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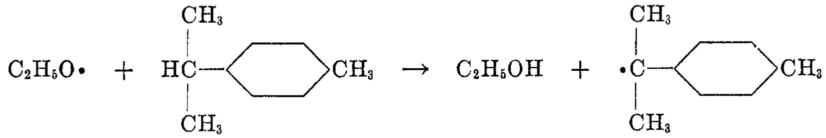
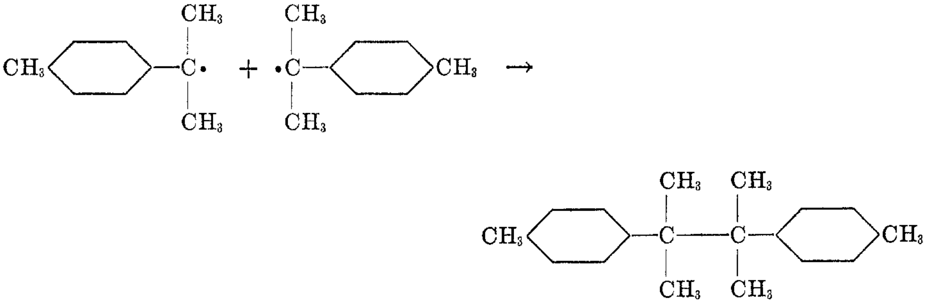
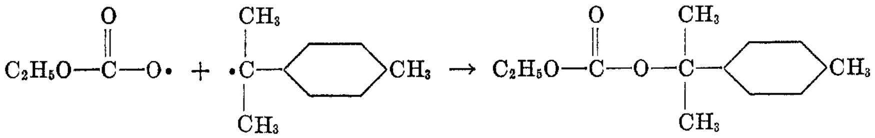
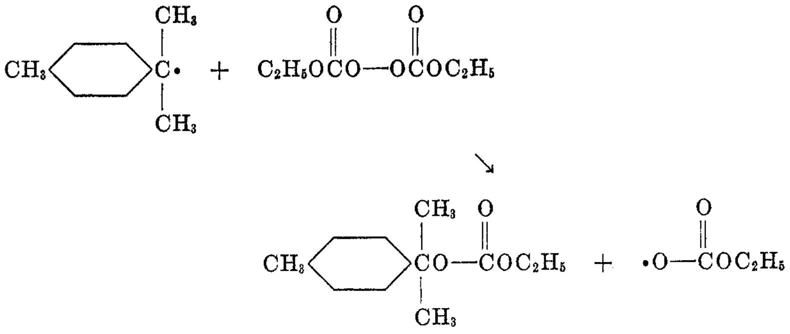
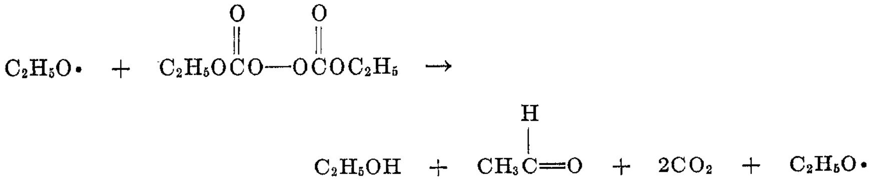
[5] Whether hydrolysis of these esters is attended by acyl-oxygen or alkyl-oxygen fission, the aromatic fragment is a particle, $R—C_6H_4(CH_3)_2C^{\mp}$ or $R—C_6H_4(CH_3)_2CO^{+}$, ($\mp$ depending on acidic or basic hydrolysis) which is well known to undergo complicating side reactions. The synthesis of esters of this type by an ionic mechanism is complicated by the fact that the alcohols, 2-phenylpropanol-2 and 2-*p*-tolylpropanol-2, are extremely sensitive to dehydration by H^+, acid chlorides, bases or salts (10). We hope to elucidate the chemistry of these esters in a later publication. They represent another class of compounds which we believe are synthesized with greater facility by free radical mechanisms than by ionic mechanisms.

II 



(a) 

(a′) 

III 

$$C_2H_5O\cdot + C_2H_5O\overset{\overset{\displaystyle O}{\|}}{C}O{-}O\overset{\overset{\displaystyle O}{\|}}{C}OC_2H_5 \rightarrow C_2H_5OH + CH_3\overset{\overset{\displaystyle H}{|}}{C}{=}O + 2CO_2 + C_2H_5O\cdot$$

This interpretation is consistent with the findings here reported for it suggests that, whenever the solvent is difficult to attack through hydrogen abstraction (II) by an alkoxy free radical, the alkoxy free radical will attack, even in dilute solution, its mother substance, the peroxide itself, to give these products of disproportionation (III).

The equations[6] below have been used in calculating percentages of H-abstraction from solvent and of disproportionation listed in Tables I and II.

$$\frac{(2 \times \text{moles of dimer} + \text{moles of ester}) \times 100}{\text{ROH}_{\text{disproportionation}} + \text{ROH}_{\text{abstraction of H from solvent}} + \text{R}\overset{\text{H}}{\text{C}}\text{=O}_{\text{disproportionation}}} =$$

$$\frac{(2 \times \text{moles of dimer} + \text{moles of ester}) \times 100}{\text{Total moles of ROH} + \text{moles of RCHO}} = \text{That percentage of all alkoxy}$$

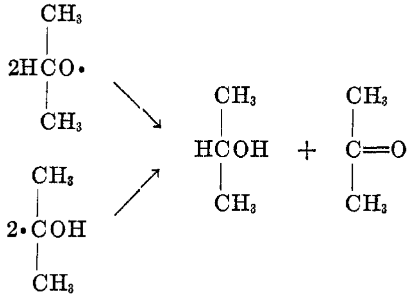
free radicals which react by abstracting hydrogen from the solvent, (scheme II).

$$\frac{\left(\text{ROH}_{\text{disproportionation}} + \text{R—}\overset{\text{H}}{\text{C}}\text{=O}_{\text{disproportionation}}\right) \times 100}{\text{Total moles of ROH} + \text{moles of R}\overset{\text{H}}{\text{C}}\text{=O}} =$$

$$\frac{2 \times \text{moles of R—}\overset{\text{H}}{\text{C}}\text{=O} \times 100}{\text{Total moles of ROH} + \text{moles of R}\overset{\text{H}}{\text{C}}\text{=O}} = \text{That percentage of all alkoxy free}$$

radicals which react by disproportionation, (scheme III). Because the mechanism of ester formation here suggested is by no means certain, the quantities of esters are reported simply as moles of ester per moles of peroxide used.

It is significant to note that these data suggest that the structurally isomeric alkoxy free radicals (2-hydroxy-2-propyl) reported by Kharasch and Friedlander (11) give rise to the same disproportionation products as the isopropoxy free radicals here reported.



In Table II below are given the data for the comparisons of the reaction of several alkyl free radicals with the reactions of their analogous alkoxy free radicals in identical solvents at approximately the same temperatures. These data on alkyl free radical reactions are taken from earlier work (4).

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[6] These mathematical equations are consistent with the provisional mechanisms here proposed for these reactions. They are nevertheless valid even if these mechanisms are incorrect, for the mathematical equations involve only quantities of products obtained from the reactions.

TABLE I[a]

REACTION DATA

REACTION: $RO\overset{O}{\overset{\|}{C}}—O\overset{O}{\overset{\|}{C}}OR$ + Solvent at t°C. •OR = Alkoxy Free Radical	MOLES OF PER-OXIDE	MOLES OF CO_2	MOLES OF ROH	MOLES OF ALDEHYDE (OR KETONE)	MOLES OF ALDE-HYDE + ALCOHOL	MOLES OF DIMER	MOLES OF ESTER[b]	MOLES OF SOLVENT: Used in exper-iment	MOLES OF SOLVENT: Re-claimed un-changed	H-ABSTRAC-TION FROM SOLVENT, %	DISPRO-PORTION-ATION, %	MOLES OF ESTER/MOLES OF PER-OXIDE
$\bullet OCH_3$ + p-Cymene (110°)	0.60	0.78	0.82	0.00	0.82	0.058	0.485	3.85	2.97	73.29	0.0	0.801
$\bullet OCH_3$ + p-Cymene (155°)	.26	.37	.45	.00	.45	.069	.17	3.53	3.03	68.4	.0	.654
$\bullet OCH_3$ + Pivalic acid (130°)	.138	.24	.190	.083	.273	.04	.00	3.85	3.66	28.9	68.1	.00
$\bullet OCH_3$ + Toluene (110°)	.10	.182	.19	.00	.19	.10	.00	5.74	4.79	100.0	.0	.00
$\bullet OCH_3$ + Cumene (110°)	.215	.30	.30	.00	.30	.045	.093	2.00	1.56	61.0	.0	.433
$\bullet OC_2H_5$ + Cumene (130°)	.36	.66	.53	.055	.58	.17	.072	2.55	1.84	70.4	18.8	.200
$\bullet OC_2H_5$ + p-Cymene (110°)	.27	.415	.46	.034	.49	.10	.09	2.33	1.84	58.7	13.7	.333
$\bullet OC_2H_5$ + Pivalic acid (140°)	.287	.54	.30	.24	.53	.015	.00	3.69	3.39	5.6	95.±	.00
$\bullet OC_2H_5$ + Methyl pivalate (110°)	.20	.313	.25	.13	.38	.016	.00	2.03	2.00	8.4	68.4	.00
$\bullet OC_2H_4Cl$ + Cumene (125°)	.126	.235	.20	.04	.24	.051	.065	2.52	2.14	69.6	33.3	.515
$\bullet OC_3H_{7(n)}$ + Cumene (125°)	.035	.048	.054	.014	.068	.022	.00	2.67	2.32	64.7	41.2	.00
$\bullet OC_3H_{7(Iso)}$ + Cumene (145°)	.62	1.10	1.00	.20[c]	1.20	.25	.12	4.20	3.05	51.7	33.3	.193
$\bullet OC_3H_{7(Iso)}$ + Pivalic acid (140°)	.502	.94	.50	.431[c]	.931	.026	.00	4.90	4.60	5.6	92.5	.00
$\bullet OC_4H_{9(n)}$ + Cumene (135°)	.257	.54	.53	.01	.54	.137	.06	2.82	1.85	61.8	3.7	.233
$\bullet OC_4H_{9(Iso)}$ + Cumene (130°)	.277	.50	.40	.02	.42	.153	.045	2.59	1.89	83.5	9.5	.162

[a] All alcohols indicated in this table have been identified by their boiling points, melting points of their naphthyl carbamates, of their dinitrobenzoate esters, and the melting points of these derivatives when mixed with authentic samples. The aldehydes and ketones have been identified by their boiling points (except formaldehyde), the melting points of their 2,4-dinitrophenylhydrazones, and the melting points of these derivatives when mixed with authentic samples. Analyses have been run on derivatives of little-known aldehydes here reported. [b] This includes only carbonate esters formed in Steps (a, a′). Esters formed from the subsequent reaction of alcohol and the solvent trimethylacetic acid are not included in this table. [c] Acetone.

TABLE II

COMPARISON OF REACTIONS OF ALKYL FREE RADICALS WITH REACTIONS OF ALKOXY FREE RADICALS

FREE RADICAL[b]	SOLVENT					
	Isopropylbenzene (A)		*p*-Methylisopropyl benzene (A′)		Trimethylacetic acid (B)	
	H-Abstraction, from Solvent, %	Disproportionation, %	H-Abstraction from Solvent, %	Disproportionation, %	H-Abstraction from Solvent, %	Disproportionation, %
(125°) A $\cdot CH_3$ (125°) A′ (125°) B	100.	0.	100.0	0.	71.0	0.
(110°) A $\cdot OCH_3$ (110°) A′ (130°) B	61.0	0.	73.3	0.	28.9	68.1
(130°) A $\cdot OC_2H_5$ (110°) A′ (140°) B	70.4	18.8	58.7	13.7	5.3	95.±
$\cdot C_3H_{7(n)}$ (125°) A (135°) B	78.0	22.0			0.–3.0	20.0[a]
$\cdot OC_3H_{7(Iso)}$ (145°) A (140°) B	51.7	33.3			5.6	92.5
$\cdot C(CH_3)_3$ (135°) A	0.	84.0				
$\cdot OC_4H_{9(Iso)}$ (130°) A	83.5	9.5				
$\cdot OC_4H_{9(n)}$ (135°) A	61.8	3.7				

[a] In trimethylacetic acid 50% yield of *n*-hexane was obtained suggesting dimerization of these initial *n*-propyl free radicals (4). [b] The temperature is indicated for the reaction of each free radical in a particular solvent.

These data indicate that for purposes of abstracting hydrogen from the solvent the alkoxy free radical serves about equally as well as its analogous alkyl free radical if the solvent molecule has readily abstractable hydrogen (Type A). If, however, the solvent molecule has all difficultly abstractable hydrogens (Type B), then the corresponding alkyl free radical gives the better results. These data suggest also that when the activation energy for a given reaction involving H-abstraction from solvent is relatively great, the alkoxy free radical shifts to a greater extent toward disproportionation (attack on parent peroxide) than does its corresponding alkyl analog.

EXPERIMENTAL

Reagents. The *chlorocarbonates* have been commercial products (Eastman Kodak Co. and U. S. Industrial Chemical Co.) and were distilled through 18-inch Vigreux columns immediately before use. The *hydrocarbon solvents* have been fractionally distilled from metallic sodium through a 20-plate column. The *trimethylacetic acid* was Eastman Kodak Company's white label product, m.p. 33°.

General procedure for handling the peroxides. In all this work the peroxides have been prepared and purified in hoods behind 1-inch Plexiglas screens. In many cases the peroxides were prepared in ethyl ether. These ether solutions were dried repeatedly over anhydrous sodium or potassium carbonate. (Calcium chloride and calcium sulfate are unsatisfactory[7] for this purpose. These salts seem to catalyze the decomposition of these peroxides. Such decompositions are autocatalytic and have attained an effervescence approaching explosive violence.) In some cases the ether was directly evaporated at reduced pressure first on a water pump and finally with a mechanical pump at 2 mm. pressure while keeping the vessel immersed in a salt-ice bath at −10°. This left the pure peroxide[8] to which the proper solvent was then immediately added. In other cases the dried ether solution was, by evaporation at 0° with the water pump, reduced to one-half its original volume and the peroxide was crystallized therefrom at −80° overnight. The supernatant ether solutions were decanted and the higher-boiling solvent in which the decomposition was subsequently to be carried out was added immediately thereto. This solution was evacuated for one to two hours at 2 mm. pressure while being immersed in a 3-gallon bucket of water at room temperature. The water reduces the collection of ice on the flask during evaporation of the ether and also serves as a reasonably satisfactory cushion in case of explosion. In still other cases the peroxides were prepared directly in the inert hydrocarbon solvent which was to be the medium for the subsequent decomposition. The technique of crystallizing these peroxides from solution gives purer products. The thermal decomposition reactions were carried out behind ½-inch Plexiglas screens. The complete apparatus used in these experiments has been described in detail elsewhere (4, 13). During the decompositions the analyzed (14) peroxide solutions were introduced beneath the surface of the heated solvents from dropping-funnels equipped with capillary stems and with water-cooled jackets to prevent the premature thermal decomposition of the peroxides before the solutions reach the vessel.

Below are given detailed descriptions of two typical experiments using the specific techniques here indicated. Detailed description of a typical experiment involving the carbonate ester is included. The experiment involving the β-chloroethoxy free radical is described in detail because of the unusual properties of the β-chloroacetaldehyde obtained. These data together with the data from all the other experiments here reported are summarized and presented in tabulated form in Table I and Table II.

The preparation of diisopropyl peroxydicarbonate. Into a 2-liter 3-neck flask equipped with a stirrer and a thermometer were added 400 ml. of diethyl ether, 300 ml. of water, and 206 g. (1.68 moles) of isopropyl chlorocarbonate. With constant stirring and while immersed in a salt-ice bath at −15° there was added to the contents of the flask in small portions over a period of 30–50 minutes 65.5 g. (0.85 mole) of sodium peroxide. The temperature was not allowed to rise within the flask above 15° during this addition. After the addition of the sodium peroxide the stirring was continued for an additional 4 hours during which time the temperature was kept below 15° and an additional 300 ml. of water was added. The ether solution was separated from the water layer and dried three times over potassium carbonate at 0°. This dried ethereal solution was concentrated to one half its original volume by evaporation of the ether on the water pump while the flask was immersed in water at 0°. This concentrated solution was left to stand overnight at −80° whereupon the peroxide crystallized in white needles. The supernatant ether was decanted and to the crystals was added 425.0 g. (4.16 moles) of trimethylacetic acid heated just to its melting point, 34°. The peroxide dissolved immediately and the solution was evacuated at 1 mm. for one hour while keeping the flask immersed in 3 gallons of water at 10–15°. Some trimethylacetic acid was lost through volatility during this operation.

The thermal decomposition of diisopropyl peroxydicarbonate in trimethylacetic acid. The evacuated solution of the peroxide in trimethylacetic acid was analyzed (14) for its peroxide content and found to contain 0.50 mole. In the reaction chamber there was introduced 76.0

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[7] Bivalent cations (Fe^{++}) have been reported (8, 12) to catalyze the decomposition of dialkyl peroxides.

[8] It is not advisable to attempt to transfer the pure peroxide from one vessel to another. In solutions of heavier solvents they are reasonably safe to handle.

g. (0.74 mole) of trimethylacetic acid and the reaction was carried out as described above while the reaction chamber was held at 135–140°. The decomposition required about three hours after which time the system was swept out with dry nitrogen gas.

The reaction mixture (503.6 g.) was transferred to a 1-liter round-bottom flask and distilled through a 6-inch Claisen head while the receiving flask was connected to the cold traps and the absorption train (4, 13) used in the decomposition reaction. A fraction (31.7 g., b.p. 82°) was collected at atmospheric pressure. The absorption train was then detached and the distillation was continued at reduced pressure. The unreacted trimethylacetic acid (465.2 g., 4.60 moles) was collected at 85°/51 mm. This trimethylacetic acid was then redistilled through a 20-inch Vigreux column, b.p. 50°/3 mm., and 24.0 g. of liquid was collected in the cold traps during this distillation. Left in the distilling flask was 3.0 g. of residue which upon recrystallization from water melted at 190°. This was identified as a,a,a′,a′,-tetramethyladipic acid by the mixture melting point (190.5°) of the material with an authentic sample of this acid.

The volatile materials collected in the cold traps during these distillations and during the decomposition were combined and fractionated repeatedly through a column of approximately 15 plates. Acetone, b.p. 57–60° (25.0 g., 0.43 mole), was obtained and identified by its 2,4-dinitrophenylhydrazone and *p*-nitrophenylhydrazone derivatives. Isopropyl alcohol, b.p. 82–83° (27 g., 0.45 mole), was obtained and identified by its 3,5-dinitrobenzoate and its N-α-naphthyl carbamate. A third fraction, b.p. 126° (6.5 g., 0.05 mole), was identified as isopropyl trimethylacetate. The soda-lime tubes used in the absorption train during this decomposition and during these preliminary distillations showed a total increase in weight of 40.6 g. equivalent to 0.94 mole of carbon dioxide.

The preparation and the decomposition of dimethyl peroxydicarbonate in isopropylbenzene. Into a 1-liter 3-neck flask equipped with a stirrer and a thermometer were added 228.4 g. (1.89 moles) of isopropylbenzene, 200 ml. of water, and 109.0 g. (1.15 moles) of methyl chlorocarbonate, b.p. 70–74°. The flask was immersed in a salt-ice bath at −15°, and 45.0 g. (0.58 mole) of sodium peroxide was added over a period of one hour while keeping the temperature within the flask below 10°. The mixture was stirred at this temperature for an additional 4½ hours with the addition of 150 ml. of water while still keeping the temperature below 10°. The layers were then separated and the organic layer was dried repeatedly over potassium carbonate. Analysis (14) showed this solution to contain 0.215 mole of peroxide.

This peroxide solution was then introduced beneath the surface of 36.0 g. (0.30 mole) of isopropylbenzene heated to 110°, and the decomposition was conducted as described above, see also (4, 13). The products isolated from this decomposition are listed in Table I.

The decomposition of diethyl peroxydicarbonate in p-cymene. A solution containing 0.27 mole of diethyl peroxydicarbonate dissolved in 241.6 g. (1.80 moles) of *p*-cymene was introduced one drop at the time beneath the surface of 70.0 g. (0.53 mole) of *p*-cymene held at 110–115° over a period of 2–3 hours. Using techniques described above the following products have been isolated: Acetaldehyde (1.5 g., 0.03 mole), Carbon dioxide (18.2 g., 0.41 mole), and ethanol, (21.2 g., 0.46 mole).

Unreacted *p*-cymene (245.6 g., 1.84 moles, b.p. 61°/12 mm., $n_D^{25.5}$ 1.4878) was reclaimed. Upon cooling to room temperature after this distillation the residue deposited white crystals from a yellow oil. These crystals (26.8 g., 0.10 mole) were separated from the oil by filtration under suction on a fritted disk. Upon recrystallization from 95% ethanol they melted at 152–154°. The melting point given in the literature (15) for 2,3-di-*p*-tolyl-2,3-dimethylbutane is 155–156°. These crystals did not depress the melting point of an authentic sample of this compound.

The yellow oil (20.0 g., 0.09 mole) was probably the mixed ester, ethyl 2-*p*-tolyl-2-propyl carbonate. The following data support this view. Saponification followed by acidification with 6 *M* HCl gave vigorous evolution of a gas which gave a precipitate upon bubbling through calcium or barium hydroxide. Ethyl alcohol was obtained from this saponification. The yellow oil decomposed upon distillation and boiled over the range, 69–85°/1 mm.

Traces (0.1 g.) of ethanol were obtained in the cold trap (−80°) during this destructive distillation. At 125–128°/1 mm. there was collected 0.8 g. of material which crystallized in condenser and proved to be 2,3-di-*p*-tolyl-2,3-dimethylbutane. The residue (12.1 g.) remaining in the distilling flask was a glassy material which did not distill. The fraction (5.5 g.) collected at 69–85°/1 mm., was then repeatedly distilled through a 12-inch Vigreux column until it had a constant b.p., 63–63.5°/0.5 mm., and constant refractive index, n_D^{26} 1.4994. The analysis and the molecular weight of this product together with its inertness suggest that it is ethyl 2-*p*-tolyl-2-propyl ether.

Anal. Calc'd for $C_{12}H_{18}O$: C, 80.85; H, 10.18; M.W., 178.

Found: C, 80.39; H, 9.58; M.W. (cryoscopically in benzene), 187.

The decomposition of di-β-chloroethyl peroxydicarbonate in isopropylbenzene. A solution containing 0.13 mole of di-β-chloroethyl peroxydicarbonate dissolved in isopropylbenzene (253.9 g., 2.11 moles) was introduced dropwise beneath the surface of 49.8 g. (0.41 mole) of isopropylbenzene heated to 125–130°. An absorption tube containing Michler's ketone on glass wool was inserted in the absorption train between the last cold trap and the first soda-lime tube (4, 13) to absorb any possible hydrogen chloride which might be formed during the reaction. Upon complete addition and decomposition of the peroxide the reaction mixture was distilled through an 18-inch Vigreux column. A first fraction (1.9 g.) was collected at 86–86.5°/745 mm., and a second fraction, 26.2 g., distilled at 130–132°. The third fraction (257.2 g., 2.14 moles), collected at 79°/70 mm., was unreacted isopropylbenzene. Remaining in the distilling flask was 27.0 g. of oily residue which deposited white crystals. These crystals (12.2 g., 0.05 mole) were separated by suction filtering on a fritted disk and upon recrystallization from 95% ethanol they melted at 115–116°. This agrees with the value (115°) recorded in the literature (16) as the melting point of 2,3-diphenyl-2,3-dimethylbutane, and these crystals did not depress the m.p. of an authentic sample of this material.

The oil (14.8 g., 0.06 mole) was considered to be the mixed carbonate ester, (β-chloroethyl 2-phenyl-2-propyl carbonate). The combined volatile materials from the cold traps of absorption train and the cold trap from the distillation together with fraction one (b.p. 86–86.5°) from the first distillation were fractionated through a 24-inch Vigreux column. A first fraction (3.0 g., 0.039 mole; b.p. 85–86°) was identified through its 2,4-dinitrophenylhydrazone derivative as chloroacetaldehyde. This derivative had m.p. 135–136°. It contained, however, no chlorine. It was analyzed by the micro Dumas method for nitrogen.

Anal. Calc'd for $C_8H_6N_4O_4$: N, 25.20. Found: N, 24.94.

(This formula, $C_8H_6N_4O_4$, is based on the loss of one mole of HCl from the expected dinitrophenylhydrazone derivative. The derivative was prepared in ethanol in the usual (17) manner.) Using the same procedure the 2,4-dinitrophenylhydrazone derivative of an authentic sample of chloroacetaldehyde was prepared. This derivative melted at 136–138°. It contained no chlorine, and its nitrogen content was determined by micro Dumas method.

Anal. Calc'd for $C_8H_6N_4O_4$: N, 25.20. Found: N, 25.06.

Equal quantities of these two derivatives were mixed, and the mixture melted at 136°. No evidence is presented in support of any specific structure of this derivative. However, this loss of one mole of HCl during the formation of this type of derivative from an α-halo-carbonyl compound has been observed elsewhere (18).

The second fraction (following chloroacetaldehyde) distilled at 130–131° (16.1 g., 0.20 mole), and was identified as β-chloroethanol. The soda-lime tubes showed a gain in weight of 10.45 g. This corresponds to 0.24 mole of carbon dioxide. The Michler's ketone showed no change in color during the reaction, and the tube containing this ketone showed no increase in weight during the reaction. No hydrogen chloride gas was evolved.

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SUMMARY

Several low molecular weight dialkyl peroxydicarbonate esters have been thermally decomposed in each of two types of solvents, namely: Type A, solvents with at least one hydrogen which is easily abstracted by free radicals, and Type B, solvents all of whose hydrogens are abstracted only with difficulty by free radicals. These decompositions are described as giving rise to alkoxy free radicals which subsequently react by abstracting an hydrogen from the solvent molecule, by disproportionation, or both. The extent of H-abstraction from solvent and/or disproportionation is dependent upon the solvent, the peroxide, and the temperature. A novel reaction has been reported which leads supposedly to the formation of unsymmetrical and thermally unstable alkyl-aralkyl esters of carbonic acid. From semiquantitative data crude generalizations have been made concerning the relative tendencies on the part of some low molecular weight alkoxy free radicals to abstract hydrogen from solvent molecules.

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