687. *The Effect of Structure of Diacyl Peroxides on the Rates of Initiation of the Polymerisation of Styrene.*

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The rates of initiation of the polymerisation of styrene by 74 diacyl peroxides have been determined. The rates of initiation by substituted dibenzoyl peroxides were increased by electron-releasing groups and decreased by electron-attracting groups. *o*-Substituents greatly accelerated the rate because of a combination of steric and polarisation effects.

Straight-chain, saturated, aliphatic diacyl peroxides showed little difference amongst themselves in initiation rate, but those possessing a radical of the allyl type decomposed very rapidly; steric effects, too, were important in some cases. The rates of initiation by unsymmetrical diacyl peroxides were intermediate between the rates found for the two symmetrical peroxides.

The primary thermal decomposition rates of substituted dibenzoyl peroxides show the same trend with changes in polarity of the substituent, and it is suggested that they may be identified with the rates of initiation of polymerisation. Preliminary results show that this is probably not so in the case of the aliphatic diacyl peroxides.

The decomposition of organic peroxides in the pure state and in solution has attracted much attention in recent years. Most studies have dealt with the mechanism of the reactions involved, and where rates of decomposition have been determined the usual analytical methods have been employed.

The rates of polymerisation of vinyl monomers may be used to calculate the primary thermal decomposition rate of the peroxide provided that the following conditions are satisfied: (*a*) The radical-induced decomposition of the peroxide should not alter the free-radical concentration of the system, and thus not affect the reaction rate. (*b*) The radicals from the peroxide must be of activity comparable with, or greater than, those derived from the monomer. (*c*) The value of k_t/k_p^2 must be known (k_p and k_t are the velocity coefficients for chain growth and for termination, respectively, in the polymerisation reaction). (*d*) The thermal polymerisation rate of the monomer, if not negligible in comparison with the catalysed rate, must be known. (*e*) There is no decomposition of the peroxide by reactions not involving free radicals.

Since the radical-induced decomposition is a transfer reaction there is no reason to believe that it changes the free-radical concentration. The radicals formed from the peroxide in the primary decomposition (A) have the same structure as those from the induced decomposition (B): hence they will possess comparable activities. It will be shown in a paper dealing with effect of peroxide structure on the radical-induced decomposition, that most peroxides produce radicals of greater activity than those from styrene.

$$(\text{R·COO})_2 \longrightarrow 2\text{R·CO·O·} \qquad \text{(A)}$$

$$(\text{R·COO})_2 + \text{R}' \longrightarrow \text{R·CO·OR}' + \text{R·CO·O·} \qquad \text{(B)}$$

Two reactions which would result in the disappearance of peroxide without influencing the polymerisation are ionic fission of the peroxide link (Leffler, *J. Amer. Chem. Soc.*, 1950, **72**, 67) and loss of peroxide as a result of some of the acyloxy-radicals recombining to form inactive products before separating sufficiently to attack the monomer. It should be possible, however, to establish whether or not these reactions are of consequence by comparison with the published data.

The above conditions being assumed to be satisfied, the rate (k_i) of initiation of polymer chains will be the same as the rate of primary decomposition. It will be related to the overall first-order velocity " constant " (k_d) by

$$k_d = k_i + k'c^x$$

where $x = 0$—$1{\cdot}0$,* k' is a constant depending on the rate of the radical-induced reaction (B), and c is the concentration of the catalyst.

TABLE I.†

Symmetrically substituted dibenzoyl peroxides.

Substituent	10^4R_e	10^6k_i	Subst.	10^4R_e	10^6k_i	Subst.	10^4R_e	10^6k_i
(H)	1·265	7·0	—	—	—	—	—	—
o-Me	2·515	27·8	*m*-Me	1·165	6·0	*p*-Me	1·570	10·9
o-OMe	5·57	138	*m*-OMe	1·430	9·0	*p*-OMe	2·050	18·5
o-OEt	5·20	119	—	—	—	*p*-OEt	2·060	18·6
o-F	1·520	10·1	*m*-F	0·910	3·6	*p*-F	1·100	5·3
o-Cl	2·580	28·2	*m*-Cl	0·910	3·6	*p*-Cl	1·110	5·4
o-Br	4·420	85	*m*-Br	0·925	3·8	*p*-Br	1·090	5·2
o-I [a]	0·026	0·11	*m*-I	0·910	3·6	*p*-I	1·110	5·4
o-NO_2	0·417	(0·8)	*m*-NO_2	0·380	(0·7)	*p*-NO_2	0·215	(0·2)
						p-Et	1·495	9·9
o-CO_2Me	1·520	10·1	—	—	—	*p*-CH_2:CH	1·215	6·5
o-O·CH_2Ph	5·20	119	—	—	—	*p*-Pr^i	1·545	10·6
						p-Bu^t	1·695	12·7
3 : 5-Me_2	1·315	7·7	3 : 4-$(OMe)_2$	1·420	8·9	*p*-Ph	1·390	8·5
2 : 3-C_4H_4 [b]	7·20	229	2 : 3-$(OMe)_2$	3·31	48	*p*-*n*-$C_8H_{17}O$	2·030	18·2
3 : 4-C_4H_4 [c]	1·330	7·8	3 : 4-CH_2O_2	0·785	2·7	*p*-OAc	1·200	6·0
3 : 5-$(NO_2)_2$	0	—	2 : 3 : 4 : 5-Cl_4	1·390	8·5	*p*-O·CO_2Me	1·165	6·3
6-Cl, 3-NO_2	0·44	(0·9)	—	—	—	*p*-CN	0·900	3·6

† Geneva notation ($CO_2H = 1$) is used for aliphatic acids (except propionic and butyric).

Aliphatic diacyl peroxides.

Peroxide	10^4R_e	10^6k_i	Peroxide	10^4R_e	10^6k_i
Diacetyl	2·14	20·2	Dihexa-2 : 4-dienoyl	2·35	24·3
Dibutyryl	2·08	19·1	Diundec-9-enoyl	2·08	19·1
Di*iso*butyryl	9·10	364	Dioleoyl	1·84	14·9
Dihexanoyl	2·06	18·6	Bis-βγ-dibromobutyryl	6·45	183
Bishexahydrobenzoyl [d]	2·62	68·5	Bis-9 : 10-dibromoundecanoyl	2·00	17·6
Dioctanoyl	2·17	20·8	Bis-9 : 10-dibromostearoyl	1·85	15·1
Dilauroyl	2·06	18·6	Bisphenylacetyl [e]	0·077	0·95
Dimyristoyl	2·06	18·6	Di-γ-phenyl propionyl	2·16	20·5
Dipalmitoyl	1·88	15·6	Dicinnamoyl	1·92	16·2
Distearoyl	1·84	14·9	Di-*p*-methoxycinnamoyl	2·08	19·1
Dibut-2-enoyl	2·53	28·2	Di-*p*-nitrocinnamoyl	0·405	(0·7)
Dibut-3-enoyl [e]	0·35	6·3	Di-5-phenylpenta-2 : 4-dienoyl	0·44	0·85

Unsymmetrical diacyl peroxides.

Peroxide	10^4R_e	10^6k_i	Peroxide	10^4R_e	10^6k_i
Benzoyl *p*-nitrobenzoyl	0·530	1·2	Benzoyl stearoyl	1·750	13·5
Benzoyl *m*-nitrobenzoyl	0·725	2·3	Adipoyl dibenzoyl [f]	1·265	7·0
Acetyl benzoyl	1·940	16·5	Dibenzoyl phthaloyl [f]	1·350	8·0

[a] 0° ($K = 1{\cdot}4 \times 10^4$). [b] Di-1-naphthoyl peroxide. [c] Di-2-naphthoyl peroxide. [d] 50° ($K = 1{\cdot}0 \times 10^3$). 20° ($K = 4{\cdot}6 \times 10^3$). [f] Examined at 0·007 mole/l. to give the same active oxygen concentration as the other peroxides.

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* The value of this exponent depends on the mechanisms assumed for the induced decomposition and termination reactions. For most peroxides in styrene, termination and transfer reactions mainly involve monomer radicals, and hence $x = 0{\cdot}5$.

The relation between k_i and the rate of polymerisation (R_c) is

$$k_i = k_t(R_c^2 - R_T^2)/2k_p^2M^2C$$

where R_T is the rate of thermal polymerisation, and M and C are the concentration of monomer and catalyst at any time.

Under constant conditions of temperature and catalyst concentration, and at the start of the reaction

$$k_i = K(R_c^2 - R_T^2)$$

In this work, $K = 440$ l.^{2} mole^{-2} sec.$^{-1}$. The temperature used was 70°, and the value of k_t/k_p^2 calculated from Bamford and Dewar's data (*Faraday Soc. Discuss.*, 1947, **2**, 313) was 850 mole l.$^{-1}$ sec.$^{-1}$. The catalyst and monomer concentrations were 0·014 and 8·28 mole/l., respectively. The value of R_T was $0{\cdot}55 \times 10^{-5}$ mole l.$^{-1}$ sec.$^{-1}$ at 70°, and was thus negligible in comparison with the reaction rates measured in this work.

Table I gives data for a number of peroxides. Some of the peroxides were so unstable that they had to be examined at temperatures below 70°; these have been indicated in the table and the appropriate values of K have been used for the calculation of k_i.

TABLE II.

	Dibenzoyl		Di-1-naphthoyl			Dibenzoyl		Di-1-naphthoyl	
Temp.	10^4R_c	10^6k_i	10^4R_c	10^6k_i	Temp.	10^4R_c	10^6k_i	10^4R_c	10^6k_i
40° [a]	0·063	0·061	0·340	2·34	60° [b]	0·480	1·43	2·660	42·8
50	0·180	0·32	1·060	11·2	70	1·265	7·0	7·20	229

$E_i = 33{\cdot}6$ kcals./mole.
$A_i = 2 \times 10^{16}$.
[a] $K = 1{\cdot}54 \times 10^3$.

$E_i = 32{\cdot}0$ kcals./mole.
$A_i = 6 \times 10^{16}$.
[b] $K = 620$.

The energy of activation for the decomposition (E_i) and the frequency factor (A_i) of dibenzoyl and di-1-naphthoyl peroxides were determined from measurements of k_i at different temperatures. The results are given in Table II.

DISCUSSION.

Substituted Dibenzoyl Peroxides.—With *m*- and *p*-substituents the results show that electron-releasing groups increase the rate of initiation by the peroxides and that the reverse effect occurs with electron-attracting groups. A plot of log $(k_i)_X/(k_i)_H$, where $(k_i)_X$ and $(k_i)_H$ are respectively the initiation rates for the substituted and the unsubstituted peroxide, against Hammett's σ factors ("Physical Organic Chemistry," McGraw Hill, 1940, p. 188) for the substituents shows clearly the influence of their polarity, though there are some irregularities (see Fig. 1).

The best line relating the data (calculated by the method of least squares) gives a value for ρ of $-0{\cdot}38$ in Hammett's equation $\log (k_i)_X/(k_i)_H = \sigma\rho$. This result is identical with that found by Swain, Stockmayer, and Clarke (*J. Amer. Chem. Soc.*, 1950, **72**, 5426), though their experimental conditions were very different. It supports the view that variations in decomposition rate result from changes in the peroxide structure and are independent of the solvent. A comparison of some of the values obtained in this investigation with those calculated from published data is given in Table III. Except where indicated, the results are from those of

TABLE III.

	$k_i \times 10^6$ (sec.$^{-1}$)		$k_d \times 10^6$ (sec.$^{-1}$)
Substituent	Published data	This investigation	
p-Methoxy	34·6	18·5	—
p-Methyl	18·0	10·9	—
p-*tert*.-Butyl	17·9	12·7	—
m-Methyl	12·9	6·0	—
Unsubstituted	12·3, 8·2 (B),[e] 8·7 (S),[e] 8·1 (S)[f]	7·0	9·9 (B),[a] 9·8 (B),[d] 9·7 (B),[b] 9·7 (B),[c] 11·4 (B),[e] 9·1 (S)[f] 6·4 (B),[c] 10·3 (S)[g]
p-Chloro	10·6	5·4	
p-Bromo	9·5	4·2	—
m-Bromo	7·6	3·8	7·6 (B)[c]
p-Cyano	6·0	3·6	—
2 : 3-C_4H_4	—	229	232 (B)[b]

[a] Bartlett and Nozaki, *J. Amer. Chem. Soc.*, 1946, **68**, 1686. [b] Author, unpublished results. [c] Brown, *J. Amer. Chem. Soc.*, 1948, **70**, 1208. [d] Hartmann, Sellars, and Turnbull, *ibid.*, 1947, **69**, 2416. [e] Cuthbertson, McClure, and Robertson, *Canad. J. Res.*, 1942, **20**, 103. [f] Mayo, Gregg, and Matheson, *J. Amer. Chem. Soc.*, 1951, **73**, 1691. [g] Redington, *J. Polymer. Sci.*, 1948, **3**, 503.

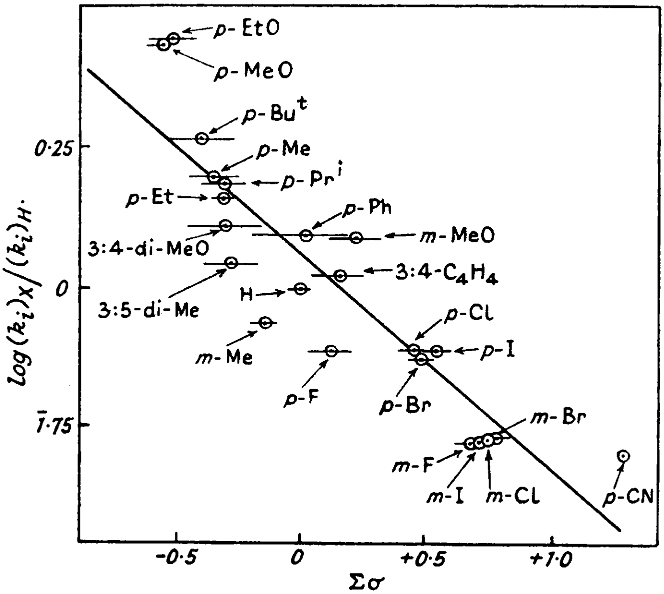
Swain *et al.* (*loc. cit.*), who used dioxan as the solvent. In the other cases the solvent is noted (B = benzene; S = styrene).

It is seen that the results observed for dioxan solutions are considerably higher than those found with other solvents or those from the polymerisation experiments. The differences could result from several causes : (*a*) The use of too low a value of k_t/k_p^2 in the calculation of k_i from polymerisation experiments. (*b*) Intrinsically higher values of k_i in the ether-type solvent. (*c*) Incomplete suppression of the chain decomposition reaction. Most of the data on dibenzoyl peroxide show that the overall decomposition rate in benzene or styrene, which includes a substantial (*ca.* 10%) term due to the induced reaction, is less than was found by Swain *et al.* (*loc. cit.*) in dioxan solution for the primary decomposition. Similar conclusions could be reached from the relative values for the di-*p*-chloro- and di-*m*-bromo-benzoyl peroxides.

There is no reason to doubt that the chain decomposition was inhibited in the decomposition reactions in dioxan, although the quoted values for E_i are somewhat low. The dielectric constant of the solvent (2·214 at 80·1°; Vaughan, *Phil. Mag.*, 1939, **27**, 669) does not suggest the likelihood of an ionic decomposition reaction of the type described by Leffler (*loc. cit.*). [The overall decomposition rate of dibenzoyl peroxide in nitrobenzene is sufficiently close to that found in benzene to indicate that ionic decomposition is of little significance (Brown, *loc. cit.*).] It would seem, therefore, that the values of k_i are affected to some extent by the solvent. The value for k_i found by Mayo *et al.* (*loc. cit.*) is comparable with that found in this investigation, and is also a measure of the peroxide actually initiating polymerisation. Mayo, however, concludes that the actual values of k_i may be higher than those found by polymerisation experiments and raises the possibility that its value may depend on the solvent used. By comparison with the results of Bartlett and Nozaki and of Mayo, the results found here would appear to be 15—25% low. This variation is quite reasonable in view of the uncertainty of the absolute values of the velocity constants of the polymerisation reaction. It is concluded that, provided that the limitations of the method are realised, the determination of k_i gives a satisfactory measure of the primary decomposition reaction.

FIG. 1.*

The horizontal lines through the points show the possible errors in the determination of $\Sigma\sigma$ (*Hammett,* loc. cit.). *The value for the* p-*cyano-grouping is that found by Roberts and McElhill* (J. Amer. Chem. Soc., 1950, **72**. 628).



* *The prefix " di " (or " bis ") is omitted throughout in the lettering.*

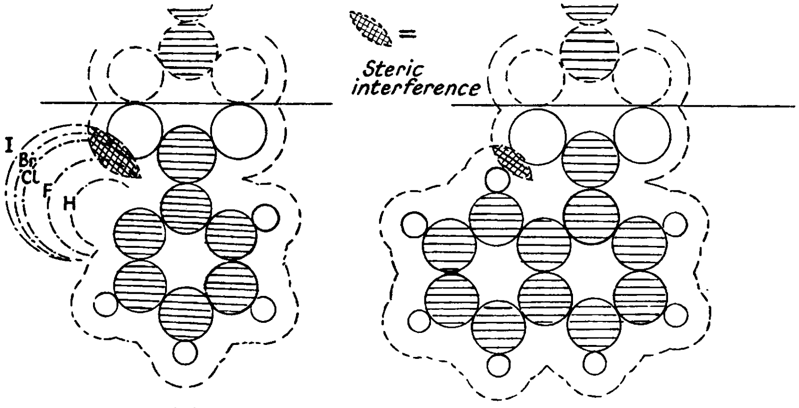
The effect of changes in polarity is in the reverse direction to that found for the alkyl hydroperoxides and dialkyl peroxides, where the stability increases with increase in the electron-releasing character of the alkyl group. Walsh (*J.*, 1948, **331**) has suggested that, although electron release would strengthen the O–O bond, too great a transfer of electron density could, by extensive overlap of the atomic orbitals, actually weaken the bond. This explanation may apply to the aromatic diacyl peroxides, but other causes may also be operative; for example, resonance stabilisation of the peroxide molecule and the radicals derived from it may be affected differently by a given substituent.

Measurements have not been made to determine whether substituents greatly influence the strength of the O–O bond. Davison (in the press) has shown that with the peroxides there is an increase in the strength of the adjacent carbonyl bond with increase in the electron-attracting character of the substituent, but it is not possible to say whether this would be accompanied by the opposite effect on the strength of the peroxide link.

The methyl group accelerates the decomposition in all orientations. As it is electron-attractive in the *m*-position, its effect, though small, is not in the expected direction. It is significant, however, that with the 2 : 3- and 3 : 4-dimethoxy-substituted peroxides, the *m*-group reduces the influence of the electron-releasing *o*- or *p*-groups.

FIG. 2.

Steric effects in o-*substituted diacyl peroxides.*



(*a*) (*b*)

Steric effects can influence peroxide stability, as is shown by the pronounced effect of *o*-substituents :

Substituent	Me	MeO	EtO	NO_2	F	Cl	Br	I [a]
Ratio of k_i, *ortho/para*	2·7	7·4	6·4	4	1·9	5·2	16·3	*ca.* 10^3

The ratio of k_i for di-1- and di-2-naphthoyl peroxides was 29·4.

[a] Estimated from the determination at 0°.

In the case of the halogens, the relation between decomposition rate and the size of the atom is readily seen, and a diagram of the molecular outlines (Fig. 2, *a*) shows considerable interference with the rotation of the molecule. The figure was constructed from the values found by Kassatochkin, Perlina, and Ablesovo (*Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **47**, 36). Their results would imply that the four oxygen atoms in the peroxide are equivalent [in a similar way to the equivalence of the four sulphur atoms in tetramethylthiuram disulphide (Craig, Davidson, Juve, and Geib, *J. Polymer Sci.*, 1951, **6**, 1)], and, therefore, that steric hindrance would be in the rotation of the aryl group about the C–C bond and not rotation of the acyloxy-group about the C–O bond. It should be pointed out, however, that the data on the structure of dibenzoyl peroxide require further confirmation. They are not consistent with the infra-red spectrum; moreover, recent (unpublished) work by Dr. I. H. Riley has shown that their interpretation of the *X*-ray crystallographic data is open to question.

The almost identical effects of the methoxy-, ethoxy-, and benzyloxy-groups in the *o*-position show that only the atoms close to the ring influence the stability; attempts to prepare a peroxide with the bulky *o*-methylthio-group were unsuccessful. Size, however, is not the only factor since the methyl group has a much smaller effect than the comparably sized iodine atom. The introduction of a second substituent markedly affects the influence of the *o*-group. This is true for many reactions where steric considerations are important (Adams and Snyder, *J. Amer. Chem. Soc.*, 1938, **60**, 1411), though in these decompositions it is not possible to differentiate between the steric and the polarisation effects. The rapid rate of decomposition of di-1-naphthoyl peroxide may thus be attributed to the rigidity of the ring structure, since the interference is relatively small (Fig. 2, *b*).

Examination of the values for the nitro-substituted peroxides shows them to be anomalously low. This is undoubtedly due to their forming radicals of low activity which inhibit the polymerisation reaction. Confirmation of this was the fall-off from linearity between the rate of polymerisation and the square root of the catalyst concentration with nitro-substituted peroxides (Cooper, *Nature*, 1948, **162**, 927). Introduction of a second nitro-substituent lowered the activity further, and bis-3 : 5-dinitrobenzoyl peroxide completely inhibited polymerisation.

A result for which no satisfactory explanation was found was the very low reaction rate of di-3 : 4-methylenedioxybenzoyl peroxide. The grouping has a normal electron-releasing character, and it would be expected to give a rate similar to that of the corresponding dimethoxy-compound. The peroxide itself had a higher melting point and was less soluble than the other alkoxy-substituted peroxides.

Di-*p*-vinylbenzoyl peroxide was peculiar in that it was copolymerised into the polymer chain. Initially a soluble, highly branched polymer was formed which contained peroxide groups; when heated, it became insoluble. The peroxide itself polymerised in the solid state or in solution to an infusible. insoluble polymer. However, the rate of fission of the peroxide link was not greatly affected by its incorporation into the polymer chain.

The temperature-dependence of k_i gave a value of E_i for dibenzoyl peroxide in good agreement with values in the literature; *e.g.*, 33·3 kcal./mole (benzene) (Nozaki and Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 1686). The increased rate of decomposition of di-1-naphthoyl peroxide results partly from an increase in the frequency factor (brought about by steric strain in the molecule), but also by a reduction in the energy of activation which is, no doubt, due to a polarisation effect.

Aliphatic Diacyl Peroxides.—The straight-chain, saturated diacyl peroxides decomposed at roughly the same rate, with a slight fall as the series was ascended. Groupings distant from the peroxide linkage had little effect on the rate, but double bonds showed a pronounced effect if they formed part of a $\cdot CH\!:\!CH\cdot CH_2\cdot CO\cdot$ grouping. When this was the case the effect was very marked; dibut-3-enoyl peroxide decomposed about 50 times as fast as the isomeric dibut-2-enoyl peroxide. The reason for this would be that the large resonance stabilisation of the allyl radical facilitates decomposition. A similar comparison may be made between bisphenylacetyl peroxide, which decomposed very rapidly because of the high resonance energy of the benzyl radical, and di-(γ-phenylpropionyl) peroxide which had a stability similar to that of an *n*-aliphatic diacyl peroxide. These observations would suggest that the free alkyl radicals were formed directly by breakdown of the peroxide and not by unimolecular decomposition of an acyloxy-radical. In support of this, it is significant that in the decomposition of aliphatic diacyl peroxides carbon dioxide is always formed, whereas with the aromatic diacyl peroxides such formation can be largely suppressed by the use of suitable conditions.

There are fewer data on the decomposition of aliphatic diacyl peroxides for comparison with the k_i values; some results are given below—they are calculated for 70°, except for the phenylacetyl peroxide (C = carbon tetrachloride, T = toluene).

Peroxide	10^6k_i	10^6k_d	Peroxide	10^6k_i	10^6k_d
Diacetyl	20·2	14·5 (C),[a] 19·0 (T) [b]	Di-(γ-phenylpropionyl)	20·5	55 (S) [d]
Dilauroyl	18·6	52 (S) [c]	Bisphenylacetyl (0°)	(1·0)	28 (T) [e]

[a] Edwards and Mayo, *J. Amer. Chem. Soc.*, 1950, **72**, 1265. [b] Ross and Fineman, *ibid.*, 1951, **73**, 2176. [c] Redington, *loc. cit.* [d] Author, unpublished result. [e] Leffler and Bartlett, *J. Amer. Chem. Soc.*, 1950, **72**, 3030.

It will be shown in a subsequent paper that these *n*-aliphatic diacyl peroxides do not react appreciably with the monomer radicals. Thus a large proportion of the dilauroyl and di-(γ-phenylpropionyl) peroxides decomposing must do so by non-radical reactions. Bisphenylacetyl peroxide apparently gives radicals of low activity, and consequently there is no relation between k_i and k_d. It is possible that some ionic breakdown of the catalyst occurs, as suggested by Leffler and Bartlett (*loc. cit.*), and some is consumed in terminating polymer chains, but the rate-determining step in the polymerisation must be the slow reaction between benzyl radicals and styrene. Conjugated double bonds, including conjugation with the carbonyl bond, had a relatively small effect. Di-(5-phenylpenta-2 : 4-dienoyl) peroxide was an apparent exception to this, but here the great resonance stabilisation would result in radicals of low reactivity, which would be inefficient in initiating polymerisation.

Steric influences apparently are important in the aliphatic series also, as shown by the rapid decomposition rate of bishexahydrobenzoyl peroxide, and of those peroxides with a methyl or a bromo-substituent adjacent to the carbonyl group. In general, apart from these cases and those where resonance-stabilised radicals may be formed, most aliphatic diacyl peroxides decomposed at substantially the same rate. Their structure, however, greatly affected their participation in the radical-induced decomposition reaction, as will be shown in another paper.

The decomposition rates of the saturated aliphatic diacyl peroxides and dibut-2-enoyl peroxide, when compared with the dissociation constants of the corresponding acids, indicate a trend in the reverse direction to that found for the aromatic diacyl peroxides. Bischloroacetyl peroxide, derived from a strong acid, has also been found to decompose very rapidly (Price, Kell, and Krebbs, *J. Amer. Chem. Soc.*, 1942, **64**, 1103).

Unsymmetrical Diacyl Peroxides.—These compounds require little comment. In all cases they had rates of decomposition intermediate between those of the two corresponding symmetrical ones. The two compounds containing two peroxide links in the molecule did not possess any unusual properties. Dibenzoyl phthaloyl peroxide decomposed at roughly the same rate as the similarly constituted di-*o*-carbomethoxybenzoyl peroxide, and the proximity of the two peroxide links did not appear to influence its stability.

EXPERIMENTAL.

Preparation of Organic Peroxides.—Most of the diacyl peroxides were prepared from the acyl chlorides and sodium peroxide solution. Some of the aromatic diacyl peroxides were readily hydrolysed or contained groupings attacked by alkali [*e.g.*, bis-3 : 5-dinitrobenzoyl peroxide and di-(*p*-methyl carbonatobenzoyl) peroxide]. In these cases the most effective reagent was 30% hydrogen peroxide and sodium hydrogen carbonate, which gave high yields of peroxide. Diacetyl peroxide was prepared by Gambarjam's method (*Ber.*, 1909, **42**, 4008). An alternative method, suitable for the preparation of small amounts of this peroxide, was to mix equal volumes of strongly cooled acetic anhydride and 90% hydrogen peroxide, the temperature being kept below −5°. Diacetyl peroxide was isolated as the upper layer on pouring the reaction mixture into cold brine.

90% Hydrogen peroxide was used to prepare dibenzoyl peroxide from benzoic anhydride at 0°, ether being used as a mutual solvent; the yields, however, were low (25—30%).

The unsymmetrical peroxides were made by shaking a solution of the appropriate acyl chloride and perbenzoic acid in chloroform with ice-cold aqueous alkali (Wieland and Razuvaiev, *Annalen*, 1930, **480**, 157). Acetyl benzoyl peroxide was prepared by the atmospheric oxidation of a mixture of benzaldehyde and acetic anhydride in the presence of a trace of dibenzoyl peroxide.

The solid peroxides were recrystallised from benzene–alcohol or benzene–light petroleum (b. p. 60—80°), the temperature being kept below 50°. Aliphatic diacyl peroxides with chains containing 8—14 carbon atoms were obtained pure by extracting the crude peroxide with alcohol, containing a little benzene if necessary, at room temperature and crystallising it at −20°. The m. p. s of new peroxides and of those for which definite values have not been established are given below.

Substituted dibenzoyl peroxides

Substituent	M. p.	Substituent	M. p.	Substituent	M. p.
p-Ethyl	58—59°	*p*-Cyano	165°	3 : 5-Dimethyl	118—120°
p-*iso*Propyl	98	*m*-Fluoro	87—88	3 : 4-Dimethoxy	119—120
p-*tert.*-Butyl	142—143	*m*-Iodo	128	2 : 3-Dimethoxy	97
p-*n*-Octyloxy	61	*o*-Methyl	54	3 : 4-Methylenedioxy	131
p-Acetoxy	120—122	*o*-Methoxy	80	2 : 3 : 4 : 5-Tetrachloro	154
p-(Methyl carbonato)	154	*o*-Benzyloxy	102	6-Chloro-3-nitro	146
p-Fluoro	93	*o*-Fluoro	66—67	3 : 5-Dinitro	158
p-Iodo	157	*o*-Bromo	108	*p*-Ethoxy	131—132

Aliphatic diacyl peroxides

Dioctanoyl	23°	Diundec-10-enoyl	23—24°	Di-5-phenylpenta-2 : 4-dienoyl	108—110°
Dilauroyl	41—42	Di(hexa-2 : 4-dienoyl)	113—114	Di-*p*-methoxycinnamoyl	93
Dimyristoyl	59	Bis-βγ-dibromobutyryl	76—78	Di-*p*-nitrocinnamoyl	140
Dipalmitoyl	67—68				

Unsymmetrical diacyl peroxides

Benzoyl *m*-nitrobenzoyl	101°	Benzoyl *p*-nitrobenzoyl	113—114°	Adipoyl dibenzoyl	93—94°
Benzoyl stearoyl	78—79			Dibenzoyl phthaloyl	119

Most of the solid peroxides were obtained highly pure and assayed at better than 98% (by the iodometric method). Liquid peroxides were dissolved in the monomer, the peroxide concentration determined in an aliquot portion, and the concentration adjusted subsequently. Solutions of the unstable bisphenylacetyl, dibut-3-enoyl, and bis-*o*-iodobenzoyl peroxides were made up at −20° to avoid serious decomposition.

Monomer Purity, and Determination of Polymerisation Rate.—The styrene was initially of 99·6% purity. It was further purified by washing it with alkaline sodium dithionite (hydrosulphite) and water, drying it, and heating it for 15 minutes at 70—80° with solid potassium hydroxide and sodium. Finally, it was distilled under nitrogen in an all-glass apparatus and had b. p. 83°/100 mm. The pure monomer was stored in the dark at −30°.

The rate of polymerisation was determined dilatometrically. The dilatometers were of 10-ml. capacity, and the volume changes were observed in a precision capillary of 1 mm. bore. They were calibrated directly by precipitating and weighing the polymer formed for an observed contraction. To facilitate cleaning and filling, the dilatometers were in two parts, the junction consisting of a cone and socket. The two parts were firmly held together by springs, and leakage of monomer was prevented by the use of a mercury seal. The rate of polymerisation was adjusted so that the heat of reaction (0·5—1·5 cal./min.) could be dissipated, and adequate temperature control maintained. The thermostat bath was kept at 70° ± 0·05°. The polymerisation was normally taken to about 3%, and over this range the rate of reaction was almost constant. A few peroxides which gave radicals of low reactivity or reacted rapidly with the styrene gave a polymerisation rate which fell off rapidly with time. In these cases the initial slope was determined.

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