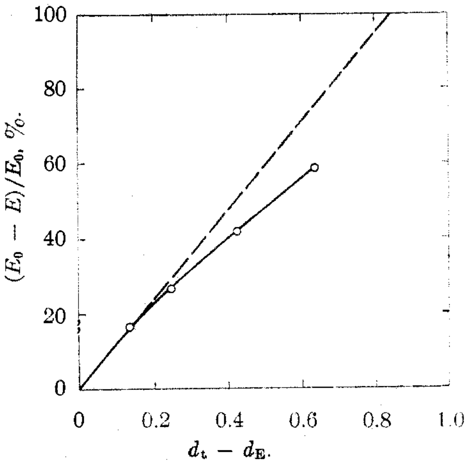


Fig. 1.—Changes in the absorption of chymotrypsin solution irradiated in air at pH 7.50, for an initial, active enzyme concentration (E_0) of 2.03 × 10^{-8} mole/ml. *cf.* equation (3).

are of course responsible for an early departure from the simple relationship, equation (3).[5] Nevertheless, equation (2) holds experimentally up to at least 80% inactivation.[6]

Summary

1. The kinetics of photochemical inactivation of chymotrypsin at 2537 Å. have been investigated. The pseudo-first order rate constant is a function of the initial enzyme concentration. The quantum yield for inactivation is virtually independent of initial enzyme concentration over a very wide range; a small change is evident at very low concentrations.

2. The quantum yield for inactivation is not dependent on phosphate buffer concentration but is different in acetate buffer.

3. Loss of activity of chymotrypsin at room temperature is parallel with loss of solubility in ammonium sulfate solution.

4. Irradiation at low temperature followed by raising the temperature of the solution to 25° gives a higher quantum yield than irradiation at 25°. Irradiation at low temperature gives a lower quantum yield for inactivation, as measured at low temperature, than is found after bringing the irradiated solution to 25°, as measured at 25°. Thus active intermediates exist at low temperature which are inactivated on warming of the solutions irradiated at low temperature.

Brooklyn, New York Received March 11, 1950

[Contribution from the Department of Chemistry, Massachusetts Institute of Technology]

Effect of Structure on the Rate of Spontaneous Thermal Decomposition of Substituted Benzoyl Peroxides

By C. Gardner Swain, Walter H. Stockmayer and John T. Clarke

The effect of structure on the rate of non-radical reactions has received considerable study. This has led to such extensive and successful quantitative relationships as the Hammett equation,[1] which by 1940 served to correlate the rates of 1763 non-radical reactions of *m*- and *p*-substituted benzene derivatives in terms of the electron-repelling or electron-attracting power of the substituent. With the 332 of these reactions which had been measured experimentally up to that time, the median deviation between calculated and observed rates was only ±15%, in spite of the fact that the variation in rate on changing from a *p*-methoxy to a *p*-nitro substituent averaged thirty-fold and exceeded a thousand-fold in several series.

In contrast, the effect of structure on the rate of free radical reactions has thus far received relatively little quantitative investigation. Nevertheless, pioneer work has been done on the "alternating tendency" in copolymerization,[2,3,4] and orientation effects in both aliphatic chlorination[5] and aromatic substitution.[6] Here also, the electron-repelling or electron-attracting power of the substituent appears to be most important in determining the rate of the reaction. To predict the effect of structural changes on the rate, it is necessary to consider the stability of the transition state. One must consider the contribution in the transition state of resonance forms involving transfer of one electron from one reactant ("donor" molecule or radical) to the other reactant ("acceptor" molecule or radical).[2,4,5] This results in a high rate when the transfer is strongly favored as a result of good electron-repelling groups in the donor or good electron-attracting groups in the acceptor. This concept is in accord with the only published application of the Hammett equation to a free radical reaction (copolymerization),[7] and it appears to be widely applicable to rates of *bimolecular* free radical reactions whether they are of the initiation, propagation, transfer or termination type.

---

(1) Hammett, *Chem. Revs.*, **17**, 125 (1935); "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, Chapter VII.

(2) Bartlett and Nozaki, This Journal, **68**, 1495 (1946).

(3) Alfrey and Price, *J. Polymer Sci.*, **2**, 101 (1947); Price, *ibid.*, **3**, 772 (1948).

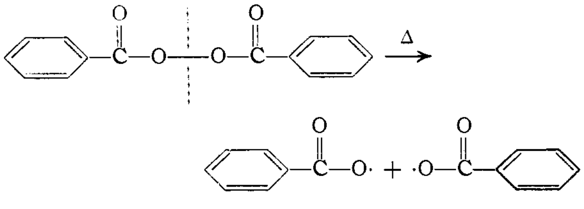
(4) Mayo, Lewis and Walling, This Journal, **70**, 1529 (1948); Walling, *ibid.*, **71**, 1930 (1949); Mayo, Abstracts of A. C. S. Organic Symposium, Madison, Wis., June 22, 1949.

(5) Ash and H. C. Brown, *Record of Chemical Progress*, **9**, 81 (1948).

(6) Hey and Waters, *Chem. Revs.*, **21**, 179 (1937).

(7) Walling, Briggs, Wolfstirn and Mayo, This Journal, **70**, 1537 (1948); Walling, Seymour and Wolfstirn, *ibid.*, **70**, 1544 (1948).

The present study was initiated to see if similar effects would be observed in a *unimolecular* free radical reaction. For this purpose we decided to investigate the effect of *m*- and *p*-substituents on the rate of spontaneous thermal dissociation of benzoyl peroxide into two benzoate free radicals. The results below will show that here quite



a different kind of polar effect dominates the rate.

Previous studies have shown that the decomposition of benzoyl peroxide, as it is usually carried out, is a complex process, involving not only a unimolecular spontaneous thermal decomposition but also a bimolecular induced chain decomposition.[8] The first experimental problem, therefore, was the search for a method for eliminating the bimolecular induced chain decomposition so that the effect of changes in structure on the unimolecular spontaneous thermal process alone could be seen.

One method which has been used to separate the spontaneous from the induced part of the decomposition involves a kinetic analysis of rate data obtained using different initial concentrations of peroxide. This assumes that the kinetic order for the induced part of the decomposition with respect to peroxide is known, is constant and is different from 1.0. Unfortunately, the kinetic order for the induced decomposition seems to be somewhat variable, thereby seriously restricting this method. Table I gives values for this kinetic order, x, in the equation

$$-\mathrm{d}P/\mathrm{d}t = k_1 P + k_i P^x$$

calculated for the reactions

$$P \xrightarrow{k_1} 2R\cdot$$

$$R\cdot + S \xrightarrow{k_2} S\cdot \text{ or } S\cdot + \left\{\begin{matrix} C_6H_5COOH \\ C_6H_6 + CO_2 \\ C_6H_5Cl + CO_2 \end{matrix}\right\}$$

$$R\cdot + P \xrightarrow{k_3} R\cdot + \left\{\begin{matrix} C_6H_5OCOC_6H_5 + CO_2 \\ C_6H_5C_6H_5 + 2CO_2 \end{matrix}\right\}$$

$$S\cdot + P \xrightarrow{k_4} R\cdot + \left\{\begin{matrix} SOCOC_6H_5 \\ SC_6H_5 + CO_2 \end{matrix}\right\}$$

and for various types of chain termination, where P stands for the undecomposed peroxide, R· for a benzoate radical, S for the solvent, S· a radical derived from the solvent, and I an inhibitor in solution in relatively constant concentration (excess). The calculated kinetic order varies from 2.0 to 0.5 depending on which type of induced decomposition (k_3 or k_4) and which type of termination is assumed to be dominant. Moreover, intermediate orders may follow from simultaneous operation of several different modes of induced decomposition or of termination. Orders of 2.0[8a,c] and 1.5[8b] have been used in applying this method for separating induced and spontaneous decomposition, but in many solvents the order experimentally found appears to be intermediate between 1.5 and 1.0. In diethyl ether as a solvent there is an exceptionally large amount of induced decomposition and the kinetics is very close to first order, which suggests that the principal kind of induced decomposition is of the S· + P (k_4) type

$$R\cdot + CH_3CH_2OCH_2CH_3 \xrightarrow{k_2} C_6H_5COOH + CH_3CH_2O\dot{C}HCH_3$$

$$CH_3CH_2O\dot{C}HCH_3 + P \xrightarrow{k_4} R\cdot + CH_3CH_2O\overset{\overset{OCOC_6H_5}{|}}{C}HCH_3$$

and the principal termination is of the R· + S· type, *i.e.*, between benzoate (R·) and ether radicals.[9]

TABLE I

CALCULATED KINETIC ORDER FOR INDUCED TERM WITH RESPECT TO PEROXIDE

Type of termination	Type of induced decomposition R· + P (k_3)	S· + P (k_4)
R· + R·	1.5	0.5
R· + S·	2.0	1.0
S· + S·	2.0	1.5
R· + I	2.0	1.0
S· + I	2.0	2.0

Uncertainty about the kinetic order of the induced chain decomposition led us to seek an effective inhibitor as a more direct method of eliminating the induced process.

Inhibition of Induced Decomposition.—Figure 1 is a semilogarithmic plot of data obtained in various pure solvents. In benzene and carbon tetrachloride the straightness of the lines indicates nearly first order kinetics, but in acetic anhydride, cyclohexane and dioxane the lines are curved, which indicates the presence of a higher order contribution.

Figure 2 shows the marked change that occurs when 1 *M* styrene is added as an inhibitor. The observed rates are now first order in all cases and vary over a much smaller range than the observed rates in the pure solvents. In the presence of 1 *M* styrene, the rates of decomposition of benzoyl peroxide in benzene and carbon tetrachloride are roughly the same as in the pure solvents; but in cyclohexane, dioxane and acetic anhydride, the presence of styrene markedly lowers the rate of decomposition. The rate curve for decomposition in pure styrene unfortunately shows a marked autocatalysis, which amounts to nearly 30% in the rate constant at the half-

---

[8] (a) D. J. Brown, THIS JOURNAL, **62**, 2657 (1940); (b) Nozaki and Bartlett, *ibid.*, **68**, 1686 (1946); (c) Barnett and Vaughan, *J. Phys. and Colloid Chem.*, **51**, 926, 942 (1947).

[9] Cass, THIS JOURNAL, **68**, 1976 (1946); **69**, 500 (1947); Bartlett and Nozaki, *ibid.*, **69**, 2299 (1947).

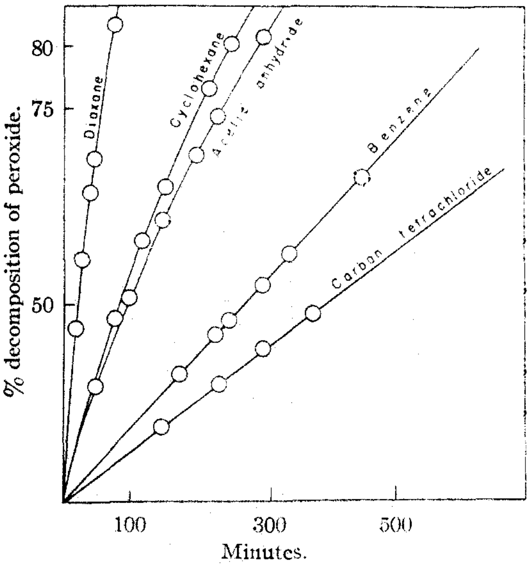


Fig. 1.—Decomposition of 0.05 M benzoyl peroxide in pure solvents at 80°.

decomposition point, and is probably due to overheating. However, the initial slope is the same as that for benzene.

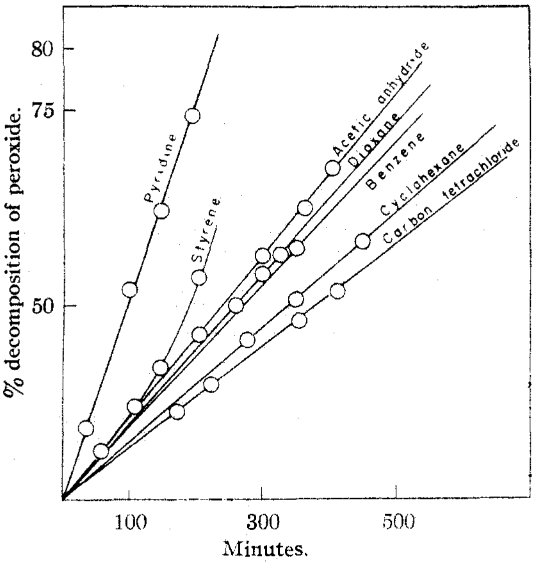


Fig. 2.—Decomposition of 0.05 M benzoyl peroxide in solvents in the presence of 1 M styrene at 80°.

As shown in Table II, the expedient of adding styrene as an inhibitor is in general more trustworthy for obtaining spontaneous rate constants than a kinetic analysis of rates measured in inhibitor-free systems. This follows from the fact that the spontaneous rate must be the slowest obtainable in any solvent, and in acetic anhydride and cyclohexane the decomposition rates for 0.05 M peroxide in the presence of 1 M styrene are substantially *lower* than the spontaneous rates deduced by Bartlett and Nozaki. Our results for benzene and carbon tetrachloride are higher than the k_1 values of Bartlett and Nozaki, but this may indicate merely that the wrong kinetic order was assumed for extrapolation to zero peroxide concentration in their kinetic analysis. Of course, extrapolation is still necessary to obtain k_1 from measurements in inhibited systems, since no inhibitor can be assumed perfect. However, it will later be seen that with good inhibitors this extrapolation is much less difficult.

Table II

First Order Rate Constants for Decomposition of Benzoyl Peroxide in Solvents at 80°

Solvent	$k \times 10^3$, min.$^{-1}$ Spontaneous constant calcd. by kinetic analysis, no inhibitor[8b]	$k \times 10^3$, min.$^{-1}$ Obsd. constant for 0.05 M peroxide plus 1 M styrene
Acetic anhydride	4.50	2.89
Cyclohexane	3.82	2.04
Dioxane	..	2.65
Benzene	1.97	2.57
Carbon tetrachloride	1.25	1.82

It should be possible to eliminate the induced chain decomposition completely by the use of a good enough inhibitor in sufficient concentration. Styrene is evidently a good inhibitor; but its efficacy was uncertain until it was compared with other inhibitors. Pure dioxane displays a relatively large amount of induced decomposition; consequently dioxane was chosen as a solvent in order to make the differences in efficiency of different inhibitors stand out more sharply.

Table III gives the half-life for decomposition of 0.05 M benzoyl peroxide in 0.2 M solutions of each of thirty-nine inhibitors in dioxane solution at 80°. Evidently, benzene, vinyl acetate and polystyrene are poor inhibitors, whereas acetanilide, triphenylmethane, nitromethane and nitrobenzene are of intermediate efficiency. The last eight inhibitors listed, including stilbene, acrylonitrile, styrene, 3,4-dichlorostyrene, 1,4-

Table III

Half-life of 0.05 M Benzoyl Peroxide in 0.2 M Solutions of Inhibitors in Dioxane at 80°

Compound	Min.	Compound	Min.
Pure dioxane	23	Triphenylmethane	75
N-Phenylsuccinimide	23	Maleic anhydride	90
Acetamide	23	1,1-Diphenylethylene	105
Ethyl acetoacetate	23	Diacetyl	110
Urethan	23	Nitromethane	115
Trioxane	23	*m*-Cresol	130
Benzene	26	*p*-Nitrotoluene	130
Anisole	27	Benzyl cyanide	175
Allyl acetate	28	Nitrobenzene	200
Toluene	28	Benzil	225
Benzamide	30	Diphenyl disulfide	225
Vinyl acetate	34	Diethyl fumarate	230
Polystyrene	35	Stilbene	270
Cumene	37	Acrylonitrile	275
Benzoic acid	40	3,4-Dichlorostyrene	275
Cyanacetamide	42	Styrene	275
Cyclohexanone	50	1,4-Diphenylbutadiene	275
Benzyl benzoate	50	Iodine	280
N-Phenylurethan	60	Methyl methacrylate	*ca.* 300
Acetanilide	70	Trinitrobenzene	*ca.* 275

diphenylbutadiene, methyl methacrylate, iodine and trinitrobenzene, are the best and are all *equally* effective in inhibiting the chain decomposition of benzoyl peroxide within the experimental error of measurement. This convergence to a limit strongly suggests that these inhibitors successfully capture all or nearly all radicals in solution to yield in their place inhibitor-type radicals which are almost incapable of attacking peroxide and which principally recombine only with other inhibitor radicals. The measured rate may thus be assumed to be close to the desired true rate of spontaneous thermal decomposition in dioxane.

However, the substituted benzoyl peroxides containing strong electron-attracting substituents such as cyano or nitro groups subsequently proved to be even more subject to induced decomposition than benzoyl peroxide. With them it was found that 3,4-dichlorostyrene is actually the best inhibitor in this group. Even it was not completely effective with the most difficult cases (nitro substituents) but it came closest to this ideal.

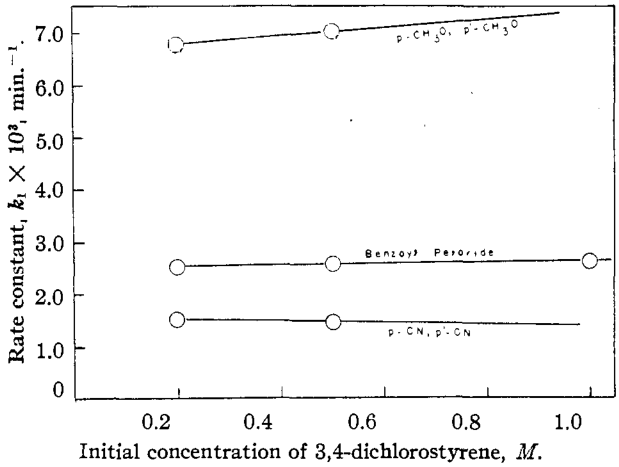


Fig. 3.—Effect of initial concentration of 3,4-dichlorostyrene on rate of decomposition of 0.05 *M* peroxides in dioxane at 80°.

Figure 3 shows the dependence of the rate constant on the concentration of 3,4-dichlorostyrene, the best inhibitor tested for the suppression of induced decomposition in dioxane. Evidently the dependence on the concentration of inhibitor is very slight provided at least 0.2 *M* is present. All the results which follow will be for dioxane solutions with 0.2 *M* concentrations of 3,4-dichlorostyrene.

Figure 4 shows the dependence on the initial concentration of peroxide. Without the inhibitor, of course, the rates are enormously greater and the dependence on peroxide concentration is very large; *i. e.*, the lines would have a steep positive slope. The constancy shown here is a strong indication that almost all of the induced decomposition has been eliminated. To be doubly sure, we have (linearly) extrapolated all our results to zero peroxide concentration and used the extrapolated figures for rate comparisons. We obtained in this way the extrapolated rate constants for sixteen different substituted benzoyl peroxides.

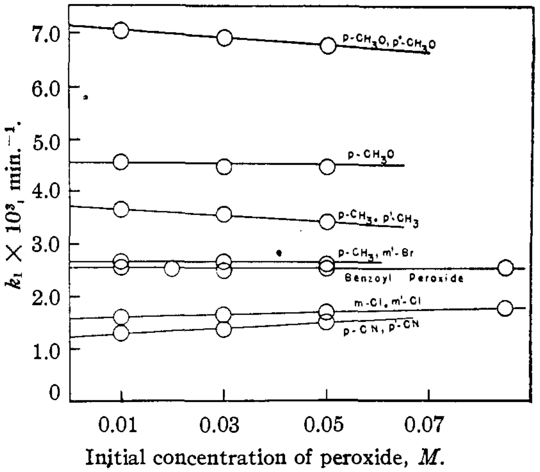
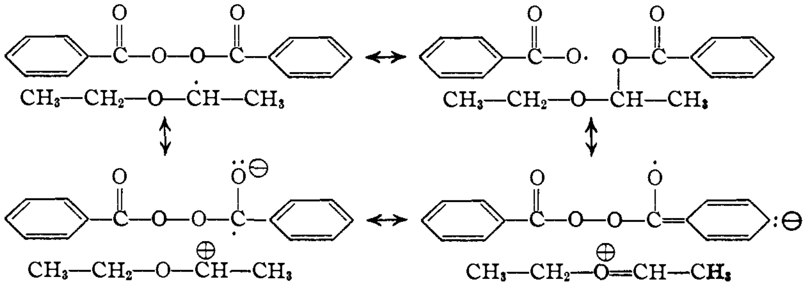


Fig. 4.—Effect of initial concentration of peroxide on rate of decomposition of peroxides in dioxane with 0.2 *M* 3,4-dichlorostyrene at 80°.

Effect of Structure on Induced Decomposition.—Induced chain decomposition of benzoyl peroxide is most rapid in ether or amine solutions.[9] Since ethoxyl and amino groups are electron donors and benzoate groups are electron acceptors, this suggests that there is important stabilization of the transition state by polar resonance structures involving transfer of an electron from the solvent radical to the peroxide. Thus the transition state in the reaction in diethyl ether (*vide supra*) may be represented as a hybrid.

Electron-attracting (*e. g.*, cyano or nitro) substituents in the peroxide make it even more susceptible to induced decomposition, because they contribute additional stabilizing resonance forms in this transition state, with negative charge on a substituent. Electron-repelling substituents (*e. g.*, methyl or *p*-methoxy) retard by hindering the electron transfer.



Benzoyl peroxide tends strongly to be an acceptor component in any electron transfer process, owing to its carbonyl groups. Therefore, the radicals which cause induced decomposition tend to be of the donor-type. The peroxide may be considered to be so reluctant to give up an electron that electron transfer in the reverse direction would not be expected to occur. The fact that solvents or solutes which would be expected to give only neutral or acceptor type radicals make good inhibitors for the induced decomposition, *e. g.*, methyl methacrylate, 3,4-dichlorostyrene, trinitrobenzene, etc., lends strong support to this concept.[10]

Polar resonance in the transition state has previously been concluded to be the dominant factor governing the change of rate with structure in other bimolecular free radical reactions studied by Bartlett, Mayo, Walling and H. C. Brown.[2,4,5]

Effect of Structure on Spontaneous Thermal Decomposition.—The Hammett equation[1] is

$$\log (k/k_0) = \rho\sigma \qquad (1)$$

where k is the rate constant for a phenyl compound containing a *m*- or *p*-substituent; k_0 is the corresponding rate constant for the unsubstituted compound; σ is a constant characteristic of only the substituent; ρ is a constant characteristic of only the reaction. Table IV and Fig. 5 show that the data on the sixteen substituted benzoyl peroxides fit the Hammett equation closely. Here the logarithm of the ratio of the rate constant with a substituted benzoyl peroxide to the rate constant for benzoyl peroxide itself is plotted against the sum of the substituent constants for the groups in the peroxide. For example, for *m*-CN the substituent constant of $+0.52$[11] is used, and for *m,m'*-dicyano twice this value (1.04) is used. The reaction constant ρ, which is equal to the slope of the line, has been evaluated as -0.38 by the method of least squares.

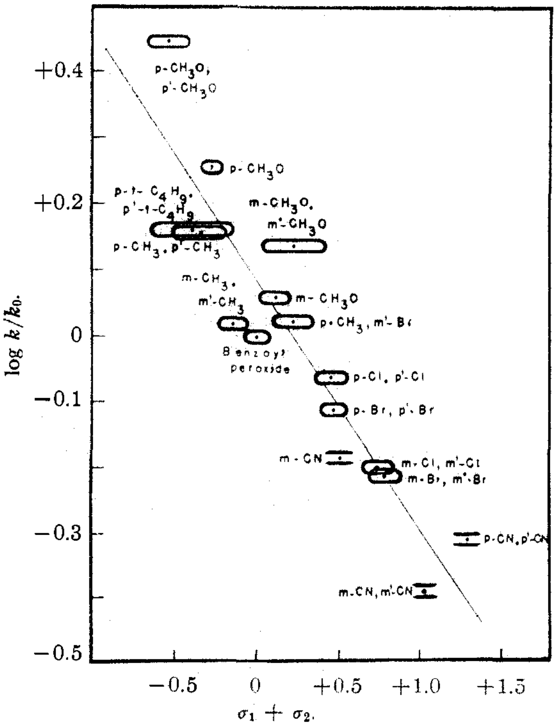


Fig. 5.—Correlation of extrapolated first order rate constants with Hammett's sigma values in dioxane solution with 3,4-dichlorostyrene at 80°.

TABLE IV

EXTRAPOLATED RATE CONSTANTS IN DIOXANE WITH 0.2 M 3,4-DICHLOROSTYRENE AT 80°

Substituents	$k_1 \times 10^3$, min.$^{-1}$	log (k/k_0)	$\sigma_1 + \sigma_2$
p,p'-Dimethoxy	7.06	0.447	−0.536
p-Methoxy	4.54	.255	− .268
p,p'-Dimethyl	3.68	.164	− .340
p,p'-Di-*t*-butyl	3.65[a]	.161	− .394
m,m'-Dimethoxy	3.45	.137	+ .230
m-Methoxy	2.89	.059	.115
p-Methoxy-*m'*-bromo	2.66	.023	.221
m,m'-Dimethyl	2.64	.019	− .138
BENZOYL PEROXIDE	2.52	.000	.000
p,p'-Dichloro	2.17	− .065	+ .454
p,p'-Dibromo	1.94	− .113	.464
m-Cyano	1.64	− .187	.517[b]
m,m'-Dichloro	1.58	− .203	.746
m,m'-Dibromo	1.54	− .215	.782
p,p'-Dicyano	1.22	− .314	1.30[b]
m,m'-Dicyano	1.02	− .393	1.03[b]

[a] Estimated from rate of decomposition in dioxane with 0.2 M styrene. [b] From K/K_0 for *p*- and *m*-cyanobenzoic acids; ref. (11).

The width of the circles represents the uncertainty in the σ constants (median deviation for other literature data[1]) and the height represents the estimated error in our rate measurements.

Activation energies were determined for only unsubstituted and *p,p'*-dimethoxybenzoyl peroxide. The values of 30.0 ± 0.3 and 29.0 ± 0.5 kcal. mole^{-1}, respectively, derived from measurements between 60 and 80°, yield entropies of activation[12] of +4.0 ± 1.0 and +3.2 ± 1.3 cal. mole^{-1} deg.$^{-1}$, indicating that these substituents exercise their effects by electronic rather than by steric interaction with the reacting center.

Electron-repelling substituents increase the rate of unimolecular spontaneous thermal decomposition, whereas electron-attracting substituents retard. This is the exact reverse of the order of susceptibility to bimolecular induced chain decomposition.

---

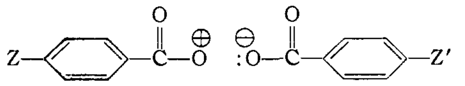
(10) Subsequent work has shown that even *p,p'*-dinitrobenzoyl peroxide will exhibit truly first order kinetics if pure nitromethane (a substance with a strong electron attracting substituent) is used as the solvent.

(11) Kilpatrick and Eanes, This Journal, **65**, 589 (1943).

(12) Glasstone, Laidler and Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., p. 199, eq. 178 (1941).

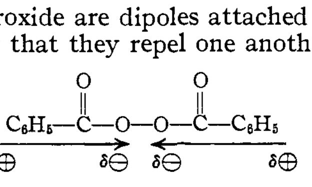
There is no minimum in the curve. This is in contrast to what one might have expected from the stability of the first formed products, *i. e.*, the benzoate radicals. Either a *p*-methoxy or a *p*-cyano group should stabilize a benzoate radical more than a *p*-hydrogen atom, since stabilizing resonance forms can be written involving either electron-repelling or electron-attracting substituents. This stabilization of radicals is demonstrated experimentally by the fact that both types of substituent (*p*-alkyl and *p*-nitro) greatly increase the concentration of triphenylmethyl radicals in equilibrium with the corresponding hexaphenylethanes.[13] This shows that the stability of the benzoate radicals forming is not the most important factor determining the rates of decomposition in dioxane.

The considerations which were so successful in explaining bimolecular free radical reactions[2–7] also seem to be inapplicable or of minor importance here. If the contribution from polar resonance forms involving transfer of an electron from one-half of the molecule to the other half



were significantly greater, or less, in the transition state than in the ground state in cases of symmetrical substitution (Z = Z′), one should expect that the difference would be amplified considerably by unsymmetrical substitution, *i. e.*, by having an electron-repelling substituent (Z) in one ring and no substituent or an electron-attracting substituent (Z′) in the other. The fact that three monosubstituted peroxides, with *p*-methoxy, *m*-methoxy and *m*-cyano as substituents, and one disubstituted peroxide with *p*-methyl-*m*′-bromo as substituents, fit the line at least as well as the symmetrical cases, *i. e.*, do not decompose abnormally fast or abnormally slowly, indicates that variation in polar resonance in the transition state of the sort discussed above is also not the most important factor determining the rate.

Only the following explanation seems to be consistent with the effect of polar substituents which is observed. The two benzoate groups in benzoyl peroxide are dipoles attached together in such a way that they repel one another. The



$$\underset{\delta\oplus}{C_6H_5}\overset{\longrightarrow}{—}\overset{O}{\overset{\|}{C}}—\underset{\delta\ominus}{O}—\underset{\delta\ominus}{O}\overset{\longleftarrow}{—}\overset{O}{\overset{\|}{C}}—\underset{\delta\oplus}{C_6H_5}$$

partial negative charges on the two central oxygens are increased by electron-repelling substituents such as *p*-methoxy and decreased by electron-attracting substituents like cyano or nitro, but not enough so that the effective charge on oxygen becomes zero or changes its sign. Therefore, *p*-methoxy groups increase the rate by increasing the electrostatic repulsion between the benzoate groups, which makes it easier for them to break apart into two benzoate radicals. The electron-attracting substituents decrease the electrostatic repulsion and make the peroxide stabler with respect to the spontaneous thermal decomposition, although in respect to the induced chain decomposition, as we have seen, such peroxides are more susceptible to attack. This argument is identical with that advanced by Lewis and Lipkin[14] to explain substituent effects on the dissociation *equilibria* of tetraphenylhydrazines, where the structural features are readily seen to be similar to those of our problem.

To give this picture more quantitative form, we note that the effective charges on the central oxygen atoms are to a first approximation linear functions of the Hammett σ-constants. The electrostatic energy between them is, therefore, proportional to $(\sigma_m - \sigma_1)(\sigma_m - \sigma_2)$, where σ_m is the Hammett constant for a hypothetical substituent which would reduce one of these charges to zero. The rate constants must then obey the relation

$$\log k = \text{const.} + \beta(\sigma_m - \sigma_1)(\sigma_m - \sigma_2) \qquad (2)$$

where β is a positive constant.[15] This may be put into the form

$$\log (k/k_0) = \rho(\sigma_1 + \sigma_2)[1 - (\sigma_m\sigma_1^{-1} + \sigma_m\sigma_2^{-1})^{-1}] \qquad (3)$$

where k_0 is the rate constant for the unsubstituted peroxide, and $\rho = -\beta\sigma_m$. It can be seen that Eq. (3) reduces to the simple Hammett relationship when both σ_1 and σ_2 are sufficiently smaller than σ_m, and this is apparently the case for the compounds we have studied. Actually, the complete Eq. (3), with $\sigma_m = 1.01$ and $\rho = -0.42$, fits the experimental results as well as (but no better than) Eq. (1) with $\rho = -0.38$.

If Eq. (3) with the above numerical constants were valid, symmetrical substitution of sufficiently powerful electron-attracting groups ($\sigma \gtrsim 1$) would cause the Hammett plot to pass through a minimum at $\sigma_1 + \sigma_2 = 2.02$, well beyond the range covered by our results. Also, unsymmetrical peroxides would be more stable than symmetrical compounds with the same value of $\sigma_1 + \sigma_2$, but again the predicted effect is too small to be detected with the unsymmetrical peroxides we have investigated.[16] It may be concluded that for most peroxides the principal factor influencing the rate of spontaneous decomposition in dioxane

---

[13] Marvel, Kaplan and Himel, THIS JOURNAL, **63**, 1892 (1941); Allen and Sugden, *J. Chem. Soc.*, 440 (1936).

[14] G. N. Lewis and Lipkin, THIS JOURNAL, **63**, 3232 (1941).

[15] Attempts to predict the numerical magnitudes of β and σ_m from detailed electrostatic models require arbitrary assumptions regarding the charge distribution in the carboxyl groups, the degree of hindrance to rotation about the single bonds, and the precise configuration of the transition state. Unfortunately, such calculations are rather sensitive to these factors, but it is possible to obtain agreement with the experimental results with an apparently reasonable, though arbitrary, model.

[16] With highly unsymmetrical peroxides, this effect will apparently be masked by the intrusion of a polar mechanism of decomposition; see Leffler, THIS JOURNAL, **72**, 67 (1950).

is the total electron density at the peroxidic linkage, irrespective of its source.

Additional support for the above considerations has been obtained from studies of the decomposition of benzoyl peroxide in a variety of solvents.[17] With the same inhibitors used in the present work, it is found that the unimolecular decomposition is slowest in non-polar solvents and is accelerated in polar solvents. For example, it was about 20% faster in toluene and 70% faster in acetonitrile than in carbon tetrachloride. This result is predicted by our model since the two polar benzoate groups are considerably more separated in the transition state than in the normal state; hence the transition state would be favored by solvent–solute interactions to a greater degree in polar solvents.

Just the opposite order of solvent effects would be predicted for the rate of dissociation of hexaphenylethane into (non-polar) triphenylmethyl radicals. In going from the normal state of a dissociating molecule to its transition state, association between solvent molecules must be disrupted to a certain extent to make room for the larger volume and surface area of the transition state. If the solvent is polar and the dissociating molecule gives non-polar fragments, this disruption will not be compensated by the accompanying increase in solvent–solute interaction, so that there will be a net increase in the work required to form the transition state, leading to a decrease in the dissociation rate. This conclusion is in accord with the observations of Ziegler and co-workers,[18] who found that hexaphenylethane dissociates in carbon tetrachloride more than three times as rapidly as in acetonitrile.

Thus, both the effect of *m*- and *p*-substituents and the effect of solvent suggest that benzoyl peroxide cleaves easily into free radicals by a unimolecular reaction largely because this relieves the electrostatic repulsion between the two benzoate groups.

Experimental

Solvents.—The benzene was Merck thiophene-free, b. p. 80.3°; and the cyclohexane, b. p. 80.8°, had been washed with fuming sulfuric acid and fractionated. Both were stored over sodium before use. The acetic anhydride, b. p. 139°, and the anhydrous pyridine, b. p. 115°, had been carefully fractionated. Carbon tetrachloride was Mallinckrodt analytical reagent. The dioxane employed was digested with dilute hydrochloric acid, freed of water with sodium hydroxide pellets, carefully fractionated, b. p. 101.5°, and stored over sodium in a plain glass bottle. It did not develop peroxides, as shown by the failure to liberate iodine from hydriodic acid, even after standing for several months on the laboratory shelf.

Inhibitors for the preliminary investigations were Eastman Kodak Co. white label chemicals, or were prepared by straightforward methods. The polymerizable inhibitors (methyl methacrylate, styrene, acrylonitrile, allyl acetate and vinyl acetate) were commercial materials which were distilled under reduced pressure and stored in a refrigerator without inhibitor. The preparation of 3,4-dichlorostyrene followed the procedure outlined by Marvel[19]: the reaction of 3,4-dichlorobenzaldehyde (Heyden Chem. Corp., New York) with methylmagnesium bromide at 0° and subsequent acetylation with acetic anhydride gave an 83% yield of α-acetoxyethyl-3,4-dichlorobenzene, b. p. 125–126° (5 mm.), which was pyrolyzed in a horizontal tube packed with glass beads at 550° to give, on fractionation, a 51% yield of 3,4-dichlorostyrene, b. p. 85.5–86.5° (5 mm.). It was stored without inhibitor in a refrigerator.

Preparation of Peroxides.—All were prepared by the reaction of a solution of an acid chloride in a hydrocarbon solvent with an excess of aqueous sodium peroxide or sodium perbenzoate at 0° with stirring.[20] This procedure is advantageous because the peroxide crystallizes as it is formed and is protected from alkaline hydrolysis by virtue of the protective wetting action of the solvent hydrocarbon.

The acid chloride was dissolved in twice its volume of hydrocarbon, preferably toluene or cyclohexane, and was added all at once to a 5% solution of sodium peroxide or sodium perbenzoate. Stirring was continued for one-half hour; and the peroxide separated as nicely formed crystals. These crystals were collected on a sintered-glass funnel and were washed well with water. Since they are likely to retain much water, they were recrystallized by rapid cooling of a filtered solution, the temperature of which did not exceed 80° at any time. The pure crystals were air-dried and were stored in a refrigerator before use. We were not able to reproduce the high yields reported by Price, in spite of wide variations in experimental conditions.

In Table V are listed the substituted benzoyl peroxides employed in this study. Also included is the solvent used for their recrystallization (followed by the approximate percentage of peroxide in the solution, in parentheses), elementary analyses, purity by titration, and physical constants of the parent acyl chloride. The appropriate pure aryl chloride and aqueous sodium perbenzoate were employed to produce peroxides 2, 4 and 16. *p*-Methyl-*m'*-bromobenzoyl peroxide, from sodium *p*-methyl perbenzoate and *m*-bromobenzoyl chloride, was chosen as an unsymmetrically disubstituted peroxide, because it was found that low yields attended attempted syntheses with *p*-methoxybenzoyl chloride and sodium *m*-bromoperbenzoate or with *p*-cyanobenzoyl chloride and *p*-methoxyperbenzoate.

In general, the melting points or decomposition points are quite sharp, and represent to a fair extent the purity of the peroxide. For example, a *p,p'*-dinitrobenzoyl peroxide of 69% purity had m. p. 151°, as opposed to m. p. 158° for the pure peroxide. Decompositions at the melting point were always quite smooth, provided that the temperature of melting was not approached with rapidity; and in no case did a peroxide detonate under the usual laboratory conditions for handling organic compounds.

Titrations.—The following procedure for the iodometric analysis of benzoyl peroxide was adopted. One-cc. to 5-cc. aliquots were pipetted into 125-cc. glass-stoppered Pyrex flasks, and 20 cc. of pure acetone added. About 2 g. of crushed Dry Ice was added to the solution to insure a slightly acid solution and to avoid possible errors due to oxygen. The flasks were warmed to room temperature with the aid of a hot-plate; 1 cc. of a half-saturated solution of sodium iodide in acetone was added and the contents of the flask swirled. The liberation of iodine was complete within a few seconds; and a gelatinous precipitate of the sodium salt of the corresponding benzoic acid was formed in some cases. After about thirty seconds, 10 cc. of carbonated water was added; and the homogeneous solution was immediately titrated with 0.01 *N* thiosulfate, made up with conductivity water. The end-points were established by comparing the run with a blank, both illuminated by a white background and a strong light.

---

[17] W. W. Vicinus, Jr., B. S. thesis, M. I. T., May, 1949.

[18] Ziegler, Seib, Knoevenagel, Herte and Andreas, *Ann.*, **551**, 153 (1942).

[19] Marvel, This Journal, **68**, 864 (1946).

[20] Price and Krebs, *Org. Syntheses*, **23**, 65 (1943).

TABLE V

TABLE OF SUBSTITUTED BENZOYL PEROXIDES

		M. p., °C. (cor.)	Analyses, % Calcd. C	Calcd. H	Found C	Found H	Solvent for recrystn.	Yield, %	Purity, %	Acid chloride, b. p., °C.	Mm.
1	*p,p'*-Dimethoxy	129 dec.[a]		[a]			Bz. (5)	62	97.5	263	
2	*p*-Monomethoxy	68–74[b]		[b]			3:1 Cyclohexane-bz. (5)	51	97.5	...	
3	*m,m'*-Dimethoxy	82.5–83.5	63.57	4.67	63.64	4.73	Cyclohexane (10)	62	99.5	245	
4	*m*-Monomethoxy	57–59	66.17	4.44	66.27	4.48	7:1 Cyclohexane–bz. (20)	68	97.5	...	
5	*p,p'*-Di-*t*-butyl	144.5–145.0 dec.	74.54	7.39	74.28	7.44	5:1 Pentane–bz. (3)	10	99.0	135	10
6	*p,p'*-Dimethyl	136–137 dec.	71.10	5.22	71.03	5.28	Bz. (10)	57	97.5	95	9
7	*m,m'*-Dimethyl	54.0–54.5	71.10	5.22	71.03	5.24	Cyclohexane (10)	40	100	88	7
8	*p*-Methyl-*m'*-bromo	90–92	53.75	3.31	54.52	3.39	Cyclohexane (10)	20	98.0	...	
9	Benzoyl peroxide	106–107 dec.[c]					2:1 MeOH–chloroform (20)	..	98.0	...	
10	*p,p'*-Dichloro	140–141 dec.[d]					1:1 Cyclohexane–bz. (10)	45	99.0	103	9
11	*m,m'*-Dichloro	122–123 dec.	54.04	2.59	54.12	2.90	Bz. (10)	60	100	228	
12	*p,p'*-Dibromo	151–152 dec.[e]					Bz. (4)	34	97.5	118	11
13	*m,m'*-Dibromo	131 dec.[e]					2:1 Bz.–cyclohexane (15)	55	97.5	118	11
14	*p,p'*-Dicyano	176 dec.	65.75	2.76	65.57	2.89	Dioxane (3)	40	98.0	132 M. p. 67–69	8
15	*m,m'*-Dicyano	163–164 dec.	65.75	2.76	65.26	2.84	Dioxane (6)	40	97.0	141 M. p. 39–41	9
16	*m*-Monocyano	101–102 dec.	67.41	3.40	67.61	3.42	1:1 Bz–cyclohexane (15)	73	97.5	...	
17	*m,m'*-Dinitro	137–138 dec.[f]					Bz. (3)	38	99.5	170	20
18	*p,p'*-Dinitro	158 dec.[f]					Bz. (2)	44	100		

[a] Vanido and Uhlfelder, *Ber.*, **37**, 3624 (1904), report 128° dec. [b] Wieland, *Ann.*, **480**, 157 (1930), report 74°. [c] Baeyer and Villiger, *Ber.*, **33**, 1574 (1900), report 106–108° dec. [d] Gelissen and Hermans, *ibid.*, **58B**, 285 (1925), found 138° dec. [e] Vanido and Uhlfelder, *ibid.*, **33**, 1047 (1900), found 152° dec. for cmpd. 12 and 132° dec. for cmpd. 13. [f] Price and Krebs, *Org. Syntheses*, **23**, 65 (1943), reported 137° dec. for cmpd. 17 and 156° dec. for cmpd. 18.

TABLE VI

TYPICAL RATE DATA IN DIOXANE WITH 0.2 M 3,4-DICHLOROSTYRENE AT 80°

Substituent	Init. concn. of peroxide, C_0, M	Time, min.	Cc. 0.01 M thiosulfate		C_0/C	$k_1 \times 10^3$ min.$^{-1}$	Av. and % dev.
None	0.05	0	19.62	19.66	1.00	..	
		251	10.47	10.47	1.88	2.51	
		324	8.65	8.65	2.27	2.54	2.53 ± 0.8
		458	6.10		3.22	2.55	
None	.009	0	8.77	8.77	1.00	..	
		225	4.91		1.78	2.55	
		316	3.90		2.25	2.56	2.55 ± 0.2
		411	3.06		2.86	2.55	
p,p'-Dimethoxy	.05	0	19.80	19.80	1.00	..	
		104	9.81		2.02	6.79	
		157	6.87		2.88	6.74	6.78 ± 0.7
		212	4.69		4.22	6.80	
p,p'-Dicyano	.05	0	20.77	20.78	1.00	..	
		410	11.11		1.86	1.515	
		536	9.16		2.26	1.52	1.53 ± 1.3
		671	7.27		2.86	1.56	

Thorough shaking of the contents of the flask at or near the end-point is essential for success, especially for heterogeneous systems likely to be encountered in the titration of peroxide decomposed in the presence of monomer or in benzene or other water-immiscible solvent.

This procedure was reproducible within ±0.5% even for titrations involving 0.001 N thiosulfate. Apparently the rate of iodination of acetone under these conditions is too slow to cause difficulties, since we found that the change of titer after dilution with carbonated water was only 4% in 30 minutes; and before dilution, the change was only 1% in the same length of time.

In the case of the solvent pyridine, the orthodox liberation of iodine from aqueous acetic acid–potassium iodide solutions was employed. Acetic acid appears to contain a considerable amount of dissolved oxygen which apparently has the power to liberate iodine; but excellent results are obtained if all air is displaced with the aid of crushed Dry Ice. About ten minutes are required for the quantitative liberation of iodine in this system.

Decompositions were carried out in sealed 15-cc. ampoules, employing 2 cc. to 12 cc. of solution. The ampoules were prepared by treating washed 18 × 150 mm. Pyrex test-tubes with a hot saturated solution of sodium hydroxide in methanol, followed by rinsing and treatment for several hours with warmed cleaning solution. After rinsing, the tubes were left standing with a very dilute solution of ammonia for a short time, then rinsed with distilled water, dried and constricted. Solutions of peroxide made up in volumetric flasks were pipetted into the ampoules, the ampoules frozen in a Dry Ice-acetone-bath while sweeping with a stream of carbon dioxide, then flushed and evacuated repeatedly with purified nitrogen, and sealed off. The sealed ampoules were warmed to room temperature and then immersed in an 80 ± 0.05° thermostat for the specified times, then removed and quenched in water. In some cases the solutions were thawed and refrozen several times under purified nitrogen before sealing off; but there were no perceptible changes in the results.

In all cases, zero-point titrations were made in order to avoid as many extraneous errors as possible. The decompositions were carried into the 50–80% range, and the results, as C_0/C, were plotted *versus* time on semilogarithmic paper. Three or more experimental points were employed to establish the rate curve for each initial concentration, and the deviations from this curve rarely exceeded ±1%. Experimental points often were titrated in duplicate; the deviation rarely exceeded ±0.2%. The greatest uncertainty was evidently the occasional lack of reproducibility of the rate curves; sometimes the variation would be as high as 5%, particularly for initial concentrations of peroxide below 0.03 *M*.

Table VI lists representative rate constants for typical runs with three peroxides and Table IV presents the rate constants for sixteen different peroxides extrapolated to zero peroxide concentration.

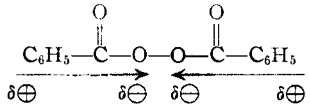
Acknowledgment.—The authors thank Swift and Company for a grant supporting this research.

Summary

1. It is possible substantially to eliminate the bimolecular induced chain process in the thermal decomposition of benzoyl peroxide at 80° in dioxane solution by adding 0.2 *M* 3,4-dichlorostyrene, which is the best of thirty-nine inhibitors tested.

2. In the *bimolecular* induced chain decomposition, electron-attracting substituents in the peroxide accelerate reaction. Stabilization of the transition state by polar resonance structures involving transfer of an electron from a solvent radical to the peroxide seems to be the dominant factor governing the change of rate with structure.

3. In the *unimolecular* spontaneous thermal decomposition, on the other hand, electron-attracting substituents retard the reaction and electron-repelling groups accelerate. The data on sixteen different *m*- and *p*-substituted benzoyl peroxides fit the Hammett equation closely. Here the most important influence governing the rate seems to be the magnitude of the coulombic repulsion between the opposing dipoles at the two ends of the molecule.



$$\underset{\delta\oplus}{C_6H_5}-\overset{O}{\overset{\|}{C}}-\underset{\delta\ominus}{O}-\underset{\delta\ominus}{O}-\overset{O}{\overset{\|}{C}}-\underset{\delta\oplus}{C_6H_5}$$

CAMBRIDGE, MASS. RECEIVED MARCH 22, 1950

[CONTRIBUTION NO. 82 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Dipole Moments of the 1,2-Dibromopropenes

BY HILTON A. SMITH AND LLOYD E. LINE, JR.

While the preparation of 1,2-dibromopropene is reported several times in the literature, only one attempt to separate the two geometrical isomers and to assign *cis* and *trans* structures to them is recorded. Van Risseghem[1] obtained a mixture of isomers by treating 1,2,2-tribromopropane with sodium phenylate in alcoholic solution. He found it impossible to separate the two isomers by fractionation procedures since isomerization took place at the boiling point of the mixture (125–133°). He did separate them by means of an azeotropic distillation with propanol, the boiling points of the two azeotropes being 95.75 and 97.05°. The isomers were recovered from the propanol solutions, and the *cis* structure suggested for the higher-boiling isomer since it showed the greater speed of dehydrobromination with potassium hydroxide.

It seemed worthwhile to check this assignment by a reliable physical method. For this reason, the two isomers were obtained, and their dipole moments measured. The results are reported here.

Experimental

Materials.—The dibromopropenes were obtained as a mixture of *cis* and *trans* isomers from the Columbia Organic Chemicals Company, Inc., of Columbia, S. C. According to information received from this company, the mixture was prepared by dehydrohalogenation of 1,2,2-tribromopropane. The materials were stored over anhydrous potassium carbonate prior to use. They were separated by fractional distillation over anhydrous potassium carbonate at about 30 mm. pressure in an eight-foot Vigreux column. The plentiful lower boiling isomer was redistilled, but the higher-boiling isomer was used without further purification. A fractionation curve is shown in Fig. 1, while the physical properties of the isomers are given in Table I.

TABLE I

PHYSICAL PROPERTIES OF THE 1,2-DIBROMOPROPENES

Isomer, boiling		Lower, *trans*	Higher, *cis*
Distillation range	°C.	40.9 ± 0.1	51.4 ± 0.2
	Mm.	28	28
$d^{30}{}_4$		1.9743	1.9900[a]
n^{20}D		1.5326	1.5282
n^{30}D		1.5275	1.5236

[a] Corrected to time of distillation.

Reagent grade (thiophene-free) benzene was fractionated through a five-foot helix-packed distillation column before use as a solvent for the determination of the dielectric constant.

Apparatus and Methods.—Because of the tendency toward isomerization[1] each benzene solution was made up and its capacitance determined as quickly as possible after collection of each sample from the still. For the first run on the higher boiling isomer, the individual samples were weighed, and the benzene solutions made from them also weighed. This caused a delay of several hours between time of collection of each sample and measurement of the dielectric constant. Subsequently, the variation in density of benzene solutions of the dibromopropenes with concentration was established. Figure 2 shows a plot of this variation. It will be noted that the points for solutions of the two isomers fit essentially the same straight line.

---

[1] H. Van Risseghem, *Bull. soc. chim. Belg.*, **28**, 376 (1919).