TABLE I

DATA CONCERNING PREPARATION OF N-(2-BROMOALLYL)-ALKYLAMINES

Primary amine reacted	Mole of Amine	Mole of 2,3-Dibromopropene	Characterization of product: Yield, %	B.p. °C.	B.p. Mm.	Nitrogen, % Calcd.	Nitrogen, % Found
Isopropylamine	6.8	2.0	68	64–67	27	7.87	7.66
n-Butylamine	10.3	5.0	74.5	71–73 cor.	10	7.29	7.12
3,5,5-Trimethylhexylamine	3.14	1.5	45	91–93 cor.	1.4	5.34	5.20

TABLE II

PHYSICAL CONSTANTS AND PERCENTAGE YIELDS OF FOUR N-ALLYLIDENE-ALKYLAMINES

Compound	B.p.,[a] °C.	Yield,[b] %	n^{25}_D	d^{25}_4	Molar refraction Calcd.	Molar refraction Found	Nitrogen, % Calcd.	Nitrogen, % Found
N-Allylidene-ethylamine	77.2–77.5	55	1.4284	0.7795	27.50	27.46	16.85	16.76
N-Allylidene-isopropylamine	93–94	57	1.4269	.7759	32.12	32.14	14.42	14.44
N-Allylidene-*n*-butylamine	129.5–130.5	77	1.4375	.7941	36.73	36.72	12.60	12.58
N-Allylidene-3,5,5-trimethylhexylamine	86.5–87.5 (10 mm.)	72	1.4489	.8113	59.83	59.93	7.73	7.83

[a] Corrected: atmospheric pressure unless otherwise indicated. [b] Based upon the N-(2-bromoallyl)-alkylamine used.

600 ml. of ether were cautiously added into the flask. The mixture was filtered, and the ethereal layer was removed and dried over solid sodium hydroxide. The product was isolated by fractional distillation of this solution.

The physical constants and percentage yields of those prepared may be found in Table II.

Acknowledgments.—The authors wish to express their appreciation to the Office of Naval Research, under whose sponsorship a portion of this project was conducted. They also wish to express sincere appreciation to Dr. J. M. Vandenbelt of Parke, Davis & Co. for determination and interpretation of the ultraviolet absorption spectra presented and to Mr. R. Bruce Scott, also of Parke, Davis & Co., for determination and interpretation of the infrared absorption spectra.

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The Reactivities of Benzaldehydes with Perbenzoate Radicals

BY CHEVES WALLING[1] AND ELIZABETH A. MCELHILL

By carrying out competitive oxidations of benzaldehydes in acetic anhydride, so that the intermediate peracids are converted to stable acetyl benzoyl peroxides, it has been found possible to develop kinetic expressions and study the relative rates of reaction of a series of benzaldehydes with various perbenzoate radicals. Relative rates have been found to increase with increasing electron donating properties of the substituents, and the results have been interpreted in terms of polar interaction between radical and aldehyde in the transition state, with contributions suggested for structures involving electron donation from the aldehyde to the perbenzoate radical. Interestingly, *n*-butyraldehyde has been found to be several times as reactive as benzaldehyde toward attack by perbenzoate radicals.

Copolymerization studies in this Laboratory and elsewhere have established that the relative reactivities of organic molecules toward free radical attack are determined both by the structure of the organic molecule and the nature of the attacking radical.[2] In particular, they have led to the recognition of the important role of the polar properties of radical and substrate in determining reaction rates in radical addition reactions, and investigations have recently been extended to include both the addition[3] and displacement[4] steps in the radical addition of mercaptans to double bonds. This paper describes a similar study of the competitive autoxidation of *m*- and *p*-substituted benzaldehydes, undertaken to determine the relation between structure and reactivity toward the peroxy radicals involved in such a process. The reaction of autoxidation was chosen because of its widespread importance and because its study yields information on the effects of substitution on both substrate and radical in a radical displacement reaction. Benzaldehydes were selected because their mechanism of autoxidation is well established, because quantitative techniques are available for analysis of the products, and because interpretation of the effects of nuclear substitution on the side chain reactions of benzene is free of complications arising from steric effects and changes in entropy of activation.[2,5]

Experimental Method.—The autoxidation of benzaldehyde possesses all the established features of a radical chain reaction—sensitivity to trace catalysis and inhibition and photocatalysis with high quantum yield.[6]

The first product of sufficient stability to permit isolation is perbenzoic acid, and the chain reaction involved in its formation presumably involves the alternating propagation steps

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[1] Lever Brothers Co., 164 Broadway, Cambridge, Massachusetts.

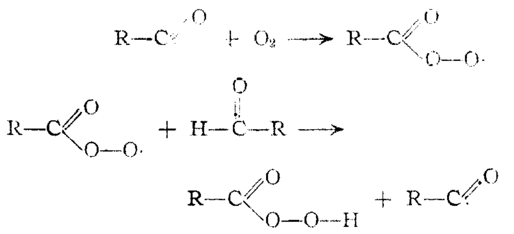
[2] F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950).

[3] C. Walling, D. C. Seymour and K. B. Wolfstirn, THIS JOURNAL, **70**, 2559 (1948).

[4] C. Walling, *ibid.*, **70**, 2561 (1948).

[5] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Ch. VII.

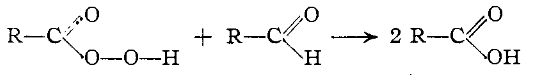
[6] For a general description and additional references, see W. A. Waters, "The Chemistry of Free Radicals," Clarendon Press, Oxford, 1946, Ch. XI.



$$\mathrm{R{-}C(=O)\cdot + O_2 \longrightarrow R{-}C(=O){-}O{-}O\cdot} \quad (1)$$

$$\mathrm{R{-}C(=O){-}O{-}O\cdot + H{-}C(=O){-}R \longrightarrow R{-}C(=O){-}O{-}O{-}H + R{-}C(=O)\cdot} \quad (2)$$

first proposed by Bäckström.[7] The ordinary autoxidation of benzaldehyde, however, is complicated by the fact that perbenzoic acid undergoes the reaction

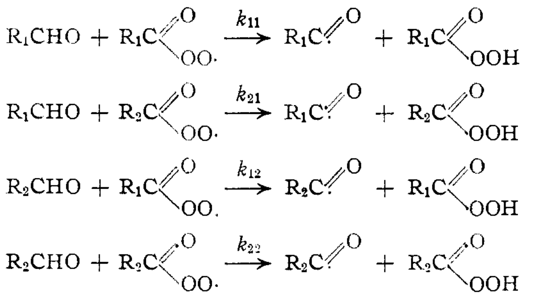


$$\mathrm{R{-}C(=O){-}O{-}O{-}H + R{-}C(=O){-}H \longrightarrow 2\,R{-}C(=O){-}OH} \quad (3)$$

so that benzaldehyde disappears by two paths.[8]

This difficulty can be obviated by carrying out the autoxidation in acetic anhydride solution (preferably in the presence of acetate ion as catalyst). Here, the intermediate perbenzoic acid is rapidly acetylated to mixed acetyl benzoyl peroxide[9] which is stable toward the aldehyde. Under these conditions, the autoxidation follows a single course and reasonably good agreement is obtained between the quantities of oxygen absorbed, titratable peroxide, and benzoic acid which can be isolated upon reducing the peroxide with iodide ion.

If a mixture of two benzaldehydes is subjected to autoxidation, and the Bäckström mechanism and long kinetic chains assumed, aldehyde disappearance is accounted for by four competing reactions.



$$\begin{aligned}
&\mathrm{R_1CHO + R_1C(=O)OO\cdot \xrightarrow{k_{11}} R_1C(=O)\cdot + R_1C(=O)OOH}\\
&\mathrm{R_1CHO + R_2C(=O)OO\cdot \xrightarrow{k_{21}} R_1C(=O)\cdot + R_2C(=O)OOH}\\
&\mathrm{R_2CHO + R_1C(=O)OO\cdot \xrightarrow{k_{12}} R_2C(=O)\cdot + R_1C(=O)OOH}\\
&\mathrm{R_2CHO + R_2C(=O)OO\cdot \xrightarrow{k_{22}} R_2C(=O)\cdot + R_2C(=O)OOH}
\end{aligned} \quad (4)$$

The kinetics thus parallel those of copolymerization[2,10] and lead to an equivalent expression for the relative rates of aldehyde consumption[11]

$$\frac{d[\mathrm{R_1CHO}]}{d[\mathrm{R_2CHO}]} = \frac{[\mathrm{R_1CHO}]}{[\mathrm{R_2CHO}]}\,\frac{r_1[\mathrm{R_1CHO}] + [\mathrm{R_2CHO}]}{[\mathrm{R_1CHO}] + r_2[\mathrm{R_2CHO}]} \quad (5)$$

where $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$. From (5) the relative rates of aldehyde consumption are determined by their relative concentrations, and two ratios of rate constants, analogous to monomer reactivity ratios, and should be independent of total concentration, over-all oxidation rate, and the presence or absence of catalysts or inhibitors. Conversely, if the relative rates of disappearance of two aldehydes are measured at two or more initial concentration ratios, a means is available for determining the values of the r's, and, accordingly, the relative reactivities of the benzaldehydes toward each perbenzoate radical. The experiments of this paper are directed toward establishing the validity of this analysis of competitive oxidations and then applying it to the determination of relative reactivities of a number of benzaldehydes toward several perbenzoate radicals.

Experimental

Materials.—*p*-Tolualdehyde and *m*-Methoxybenzaldehyde were conveniently prepared by the Rosenmund reduction of the corresponding acid chlorides, essentially as described in "Organic Syntheses."[12] ***p*-Cyanobenzaldehyde** was obtained by oxidizing *p*-tolunitrile following a procedure described for *p*-nitrobenzaldehyde.[13] ***m*-Tolualdehyde** was prepared in two steps from *m*-toluidine, by Sandmeyer conversion to the nitrile,[14] followed by reduction with stannous chloride, using a procedure described for β-naphthaldehyde.[15] ***p*-Methylmercaptobenzaldehyde** was obtained in four steps from *p*-nitrotoluene[16] by initial oxidation–reduction to *p*-aminobenzaldehyde with sodium polysulfide,[17] followed by successive conversion to *p*-thiocyanobenzaldehyde, *p*-mercaptobenzaldehyde, and final product essentially as described by Friedlander and Lenk,[18] except that the mercaptan was not isolated, but directly methylated in solution with dimethyl sulfate. The methylmercaptobenzaldehyde was finally obtained as a colorless oil, b.p. 112–117° (3 mm.) (lit. 273° (760 mm.)[18]). **Other aldehydes** were commercial materials, freshly distilled or recrystallized from ethanol (as appropriate) before use.

Oxidations were carried out in flat-bottomed vessels of approximately 25-ml. capacity (made by shrinking down the upper portion of 50-ml. Erlenmeyer flasks and sealing on 10/30 ground glass joints), attached to gas burets and mechanically shaken in a 30° thermostat. The vessels were loaded with known quantities of aldehydes, usually 1:3 and 3:1 molar ratios (approximately 4 g. total weight), 10.0 ml. of acetic anhydride, and approximately 50 mg. sodium or potassium acetate, flushed with oxygen, and connected to the oxygen-filled burets. The purpose of the acetate was to catalyze the acetylation of the peracids, since it was found that, in its absence, benzaldehyde–*p*-chlorobenzaldehyde mixtures gave low peroxide titrations and high yields of acids, presumably through peracid oxidation of the aldehydes. In fact, on cooling such oxidized mixtures actually deposited silky needles of what was apparently unacetylated *p*-chloroperbenzoic acid. Oxidations were interrupted when approximately 200 ml. of oxygen had been absorbed, and, in order to carry out the reaction in a convenient time (0.5 to 3 hours), reaction was generally speeded by illumination of the oxidation vessels by a Hanovia H-3 mercury-vapor lamp at a distance of eight inches (the radiation passing through two layers of Pyrex glass and the intervening water). The light produced a considerable acceleration, the oxidation time for a 3:1 benzaldehyde–*p*-chlorobenzaldehyde mixture being shortened from 57 to 25 minutes. No attempt was made to make precise measurement of oxidation rates, which were appreciably autocatalytic, and depended somewhat upon shaking rates. However, qualitative observations of relative rates obtained under the same conditions do permit some generalizations given in the discussion.

Isolation and Analysis of Products.—As soon as the desired quantity of oxygen had been absorbed, an oxidation was interrupted by stopping shaking, disconnecting the flask and displacing the remaining oxygen with carbon dioxide by adding a small piece of Dry Ice. The reaction mixture was next transferred to a 25.00-ml. volumetric

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[7] H. L. v. Bäckström, *Z. physik. Chem.*, **B25**, 99 (1934).

[8] A. Baeyer and V. Villiger, *Ber.*, **33**, 1569 (1900).

[9] W. R. Jorissen, *Z. physik. Chem.*, **22**, 34 (1897).

[10] F. R. Mayo and F. M. Lewis, This Journal, **66**, 1594 (1944).

[11] In order to obtain (5), steady state expressions for two radicals rather than one must be considered. However, it can easily be shown that they reduce to $k_{12}\left[\mathrm{R_1C(=O)OO\cdot}\right][\mathrm{R_2CHO}] = k_{21}\left[\mathrm{R_2C(=O)OO\cdot}\right]$ $[\mathrm{R_1CHO}]$ equivalent to the copolymerization case.

[12] E. B. Hershberg and J. Cason, "Organic Syntheses," **21**, 84 (1941).

[13] S. V. Lieberman and R. Connor, *ibid.*, Col. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 441.

[14] H. T. Clarke and R. R. Read, *ibid.*, Vol. I, p. 514.

[15] J. W. Williams, *ibid.*, **23**, 63 (1943).

[16] The authors are indebted to Mr. V. C. Simpson of the General Laboratories for carrying out this preparation.

[17] H. G. Beard and H. H. Hodgson, *J. Chem. Soc.*, 4 (1944).

[18] P. Friedlander and E. Lenk, *Ber.*, **45**, 2087 (1912).

flask, and made up to volume with acetic acid. Two 2.00-ml. aliquots were titrated for peroxide by adding each to 25 ml. of acetic acid in an iodine flask from which air had been displaced by carbon dioxide, introducing 1.0 ml. of saturated potassium iodide solution, and after fifteen minutes, diluting with water and titrating to a starch endpoint with 0.05 *N* sodium thiosulfate. The balance of the contents of the volumetric flask was next transferred, with the aid of a few cc. of chloroform, to a 500-cc. separatory funnel from which air had been displaced by carbon dioxide. The mixed acetylbenzoyl peroxides were reduced by adding 10 ml. of saturated potassium iodide solution and letting stand ten minutes. The liberated iodine was next reduced with 20 ml. of 2 *N* sodium sulfite solution, the mixture diluted to roughly 250 ml. and brought to *p*H 9 by addition in small portions of approximately 80 ml. of 5 *N* sodium hydroxide. Considerable heat was evolved at this stage by the hydrolysis and neutralization of acetic anhydride, and the separatory funnel was cooled between additions of alkali by shaking under a water tap. Unreacted aldehydes were next extracted with two small portions of chloroform, and the funnel contents acidified (*p*H < 4) with 12 *N* hydrochloric acid.

In the first series of experiments on benzaldehyde–*p*-chlorobenzaldehyde used to establish the validity of the method, the mixed acids were separated by extraction with three (approximately 25-ml.) portions of chloroform, collected in a tared 125-ml. Erlenmeyer flask containing a boiling chip and isolated by evaporating the solvent on a steam-bath followed by drying to constant weight (1–2 hours) *in vacuo*. In a blank experiment using 1.023 g. of benzoyl peroxide in 10 ml. of acetic anhydride, an amount of benzoic acid was isolated corresponding to 1.032 g. after correcting for the two aliquots taken for titration. Later it was found that the isolated acids sometimes contained traces of inorganic salts, so that the isolation procedure was modified in that the chloroform extract containing the acids was collected in a 125-ml. filter flask, taken to dryness, and the acids purified by sublimation *in vacuo* to a cold-finger inserted in the neck of the flask. In blank experiments 96% of a benzoic acid sample was recovered after sublimation, and a benzoic–*p*-chlorobenzoic acid mixture analyzing for 6.53% Cl gave a sublimate containing 6.40% Cl.

In the case of the competitive oxidation of *p*-chlorobenzaldehyde–*p*-cyanobenzaldehyde, the above procedure was modified in that the (very insoluble) mixed acids were separated from the acidified solution by simple filtration rather than extraction, washed, and dried. Similarly, with the *p*-chlorobenzaldehyde–*n*-butyraldehyde system the *p*-chlorobenzoic acid was filtered off, washed and dried, and the yield of butyric acid calculated by difference from the amount of oxygen consumed.

Following isolation, mixed acids were weighed and their compositions determined by halogen analysis with the exception of benzoic–anisic acid mixtures where Zeisel methoxyl determination was employed. Results of all significant experiments are listed in Table I.

The reasonably quantitative nature of the reaction is indicated by the fact that the median deviation between oxygen absorbed and peroxide titrated is 3.5%, the peroxide usually being high, perhaps due to further oxidation during manipulation. Yields of acids were in general a little lower than that calculated from oxygen consumed (median, 5%). However, analysis of the data on the benzaldehyde–*p*-chlorobenzaldehyde system indicated that the losses were not appreciably selective and there was no significant difference between the analyses of acid mixtures recovered in good yield and mixtures where recovery was relatively low. Further, no significant differences in composition were observed between mixtures oxidized slowly in the dark or more rapidly in the presence of light.

TABLE I

COMPETITIVE OXIDATIONS OF SUBSTITUTED BENZALDEHYDES AT 30° (ALL QUANTITIES IN MILLIMOLES)

Initial millimoles of aldehydes with indicated substituents		Time. hr.	O_2 absorbed	Yield Peroxide found	Yield Acids isolated	Mole %, Cl acid in product
H	*p*-Cl					
9.75	21.50	2.0	8.47	8.43	7.97	57.0
19.55	14.46	1.5	8.63	8.59	9.05	29.3
29.30	7.23	1.25	8.63	8.74	9.08	13.12
9.75	21.32	2.25	8.64	8.67	7.83	59.8
9.75	21.50	2.0	8.48	8.48	8.02	58.1
19.55	14.69	2.0	8.48	8.38	7.10[a]	32.3
19.55	14.54	2.0	8.67	8.67	7.60	33.3
29.30	6.98	1.5	8.44	8.54	8.24	13.8
29.30	7.27	1.25	8.60	8.67	8.12	14.1
p-Cl	*p*-CH$_3$					
24.95	8.33	2.17	8.67	8.31	8.51	55.0
25.0	8.34	3.17	8.52	9.29	9.37	54.1
24.95	8.34	3.20	8.69	9.27	7.42	53.2
8.29	25.1	1.17	8.65	8.33	..	13.98
8.04	25.1	0.83	8.64	8.35	7.61	13.4
p-Cl	*p*-CH$<^{\mathrm{CH_3}}_{\mathrm{CH_3}}$					
19.51	6.47	0.83[b]	8.58	8.38	8.76	58.7
19.52	6.47	3.63	8.70	8.31	8.38	58.0
6.39	19.58	3.58[b]	7.75	7.50	7.18	16.4
6.42	19.58	0.83	8.47	8.42	8.13	14.51
6.84	19.58	0.92	8.46	8.40	7.24	15.68
H	*m*-Cl					
29.2	8.66	0.70	8.49	8.56	7.80	13.65
29.2	8.66	0.30	8.65	8.87	8.90	13.55
9.70	26.0	..	8.58	8.39	8.74	57.4
9.70	26.0	0.83	8.50	8.34	7.72	56.5
p-Cl	*p*-OCH$_3$					
24.2	8.07	2.70	8.58	8.04	8.34	48.9
24.15	8.07	1.03	8.85	8.92	8.72	48.2
29.1	8.07	1.43	8.67	9.03	7.91	50.4
8.05	24.4	2.50	8.45	8.60	6.74	13.13
8.10	24.38	3.00	8.77	8.22	7.72	11.95
p-Cl	*m*-CH$_3$					
25.1	8.37	1.20	8.49	8.24	8.19	56.8
25.1	8.37	1.20	8.56	8.42	8.48	57.6
5.71	16.71	3.42	8.74	8.20	7.29	14.95
8.34	25.2	2.12	8.66	8.16	7.97	14.37
p-Cl	*p*-CN					
23.3	7.73	0.83	8.48	8.71	8.21	80.6
21.25	6.87	1.42	8.48	8.48	8.48	76.1
23.7	7.60	0.62	8.86	8.48	8.87	74.7
22.95	7.57	1.25	8.47	9.04	8.71	81.0
7.53	22.85	2.97	8.51	8.02	8.70	34.8
7.58	22.9	2.42	8.68	7.98	7.47	44.1
7.15	23.4	2.08	8.66	8.23	7.74	33.0
7.45	22.9	1.75	8.66	7.98	6.72	27.1
H	*p*-OCH$_3$					
29.15	8.06	1.70	8.40	9.25	8.67	23.4[c]
29.15	8.06	1.65	8.56	9.71	9.13	23.4
29.1	8.23	0.97	8.67	9.76	8.48	27.4
29.1	8.23	1.00	8.84	9.25	7.66	28.8
9.70	24.35	4.17	8.25	9.30	8.19	80.7
9.70	24.35	4.08	8.59	9.74	8.17	80.7
9.88	24.4	5.22	7.70	7.86	6.77	81.8
p-Cl	*n*-Butyraldehyde					
33.15	11.01	0.72	8.98	9.83		35.0
32.9	11.01	.55	8.58	8.66		37.5
11.05	33.15	.50	8.55	10.32		3.65
11.02	33.15	1.27	8.75	9.41		3.72

[a] Some of product lost. [b] Photoflood light used, instead of mercury arc. [c] Mole % anisic acid in product, calc. using empirical value of 19.91% OCH$_3$ (found in blank analyses) for pure anisic acid (theory 20.35%).

TABLE II

REACTIVITY RATIOS IN COMPETITIVE OXIDATIONS OF ALDEHYDES AT 30°

Aldehyde (1)	r_1	Aldehyde (2)	r_2
p-Chlorobenzaldehyde	0.146 ± 0.020	Anisaldehyde	2.36 ± 0.02
p-Chlorobenzaldehyde	.236 ± .023	*p*-Tolualdehyde	2.15 ± .07
p-Chlorobenzaldehyde	.335 ± .077	*m*-Tolualdehyde	2.20 ± .03
p-Chlorobenzaldehyde	.285 ± .035	*p*-Isopropylbenzaldehyde	1.87 ± .18
p-Chlorobenzaldehyde	1.15 ± .38	*p*-Cyanobenzaldehyde	0.46 ± .27
p-Chlorobenzaldehyde	0.540 ± .08	Benzaldehyde	1.62 ± .12
m-Chlorobenzaldehyde	0.378 ± .024	Benzaldehyde	1.95 ± .28
Anisaldehyde	2.22 ± .16	Benzaldehyde	1.00 ± .14
p-Chlorobenzaldehyde	0.278 ± .056	*n*-Butyraldehyde	10.73 ± .42

Treatment of Data.—Relative reactivities of aldehydes were determined by the graphical solution of the integrated form of eq. (5) as previously described[2,10] using, in every case, oxygen absorption as the measure of extent of reaction. Figure 1 is a plot of the data for benzaldehyde–*p*-chlorobenzaldehyde, and illustrates the consistency of the data. Plots for other systems have been omitted in the interests of brevity, and values of *r*'s are listed in Table II. The possible sources of error include side-reactions, both in the oxidation and in the reduction of the peroxide, losses, contamination of the isolated acids, and analytical error. In some cases (notably the *p*-chloro-*p*-cyanobenzaldehyde and benzaldehyde–anisaldehyde systems) duplicate sets of experiments showed better internal agreement than agreement with each other. Under the circumstances, the standard deviation of duplicate experiments has been given as the experimental error in Table II with the realization that some systems may contain systematic errors as well. Errors in derived quantities were calculated from the errors in *r*'s using the usual formulas.

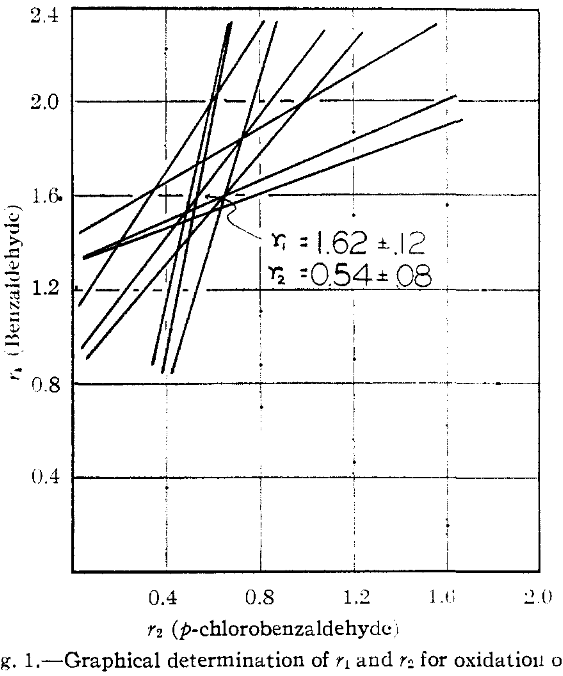


Fig. 1.—Graphical determination of r_1 and r_2 for oxidation of the benzaldehyde–*p*-chlorobenzaldehyde system.

Results and Discussion

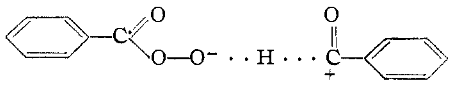
Relative reactivities of the various benzaldehydes toward the *p*-chloro-, *p*-methoxy- and unsubstituted perbenzoate radicals have been calculated from the data of Table II, and are listed in Table III, taking in each case the reactivity of benzaldehyde itself as unity. The aldehydes have been listed in order of increasing Hammett σ value of the substituents and it is evident that reactivities in general decrease with increasing electron withdrawal by the substituent.

TABLE III

RELATIVE REACTIVITIES OF SUBSTITUTED BENZALDEHYDES TOWARD INDICATED PERBENZOATE RADICALS

Benzaldehyde	σ	Perbenzoate radical Unsubst.	*p*-Cl	*p*-OCH_3
p-OCH_3	−0.268	1.00 ± 0.141	3.70 ± 0.54	2.21 ± 0.16
p-CH_3	− .170	....	2.29 ± .41	....
p-C_3H_7	− .151	....	1.90 ± .37	....
m-CH_3	− .069	....	1.61 ± .44	....
Unsubst.	0	1.00	1.00	1.00
p-Cl	.227	0.618 ± .046	0.540 ± .08	0.937 ± .094
m-Cl	.373	0.513 ± .074	....	....
p-CN	1.000	....	0.469 ± .167	....

In copolymerization and radical addition studies, effects of substituents on reactivity have in general been successfully discussed in terms of resonance stabilization of radicals produced, polar phenomena, and steric effects, the last being dismissed when, as here, substitution is at a point remote from the site of reaction.[2] If we apply the same criteria to our competitive aldehyde oxidations, it follows that the chief factor determining the effect of substituents must be a polar phenomenon rather than radical stabilization, since both –Cl and -CN substituents, which should stabilize the benzoyl radicals resulting from hydrogen removal from the aldehydes, decrease reactivity. Further, this together with the increased reactivity produced by electron supplying groups (alkyl and -OCH_3) indicates that here we are dealing with a donor molecule and an acceptor radical. Paralleling the treatment of other radical reactions, this suggests the participation of polar structures such as



to the transition state, a reasonable hypothesis since the forms involved are the relatively stable perbenzoate and benzoyl carbonium ions.

The data of Table III suggest further conclusions. The increase in reactivity with introduction of *p*-CH_3 and *p*-OCH_3 (2.3 and 3.7 fold toward the *p*-chloroperbenzoate radical) lies between that observed for styrenes toward methacrylate-[19] and maleic anhydride-type[20] radicals. The system is thus one showing a moderate polar effect, much less

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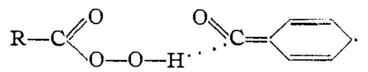
[19] C. Walling, E. R. Briggs, K. B. Wolfstirn and F. R. Mayo, THIS JOURNAL, **70**, 1537 (1948).

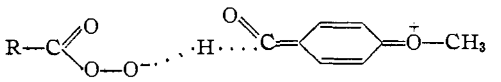
[20] C. Walling, D. C. Seymour and K. B. Wolfstirn, *ibid.*, **70**, 1544 (1948).

than that observed in the addition of thioglycolic acid to α-methylstyrene.[3]

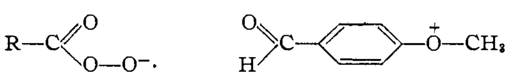
Further significant relations among the data of Table III are brought out when the logarithms of the relative reactivities of the aldehydes toward the *p*-chloroperbenzoate radical are plotted against the σ values of the substituents (Fig. 2). As in the case of other acceptor radicals,[2] strongly electron donating groups show an enhanced effect, and all points do not lie on a single straight line. In addition, for the first time in a side chain radical reaction of benzene, substituents which withdraw electrons but stabilize radicals (*i.e.*, *p*-Cl and *p*-CN) produce appreciably lower reactivity, suggesting that, somehow, in attack on benzaldehyde, the substituents are able to make little contribution to the stability of the transition state. This peculiarity is further emphasized when the reactivities of benzaldehyde and *n*-butyraldehyde are compared (*cf.* Table II). Butyraldehyde is roughly twice as reactive toward the *p*-chloroperbenzoate radical, although the phenyl group of benzaldehyde should provide extensive resonance stabilization of the resulting benzoyl radical. A possible explanation is that contributions from such *radical stabilizing* resonance in the transition state, involving structures with an odd electron spread over the benzene ring, *i.e.*



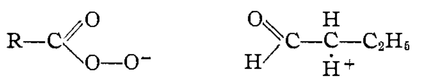
require a linear configuration of carbonyl group and benzene ring which might be sterically impossible in the transition state, but can occur in the free radical. Similarly, additional structures involving the substituents might also be ruled out. Such a steric restriction would also decrease the number of *polar* forms in the transition state, ruling out some structures such as



but permitting



and



and might account for the only moderate polar effects observed.

Figure 1 also includes data on relative reactivities towards the perbenzoate and *p*-methoxyperbenzoate radicals. Comparison of relative reactivities, as judged by the slopes of the lines of Fig. 2 and also by the additional data on the other perbenzoate radicals contained in Table II, show the polar properties of all the radicals to be similar, but differing some in degree. The only anomalous result is the similar reactivity of benzaldehyde and anisaldehyde toward the unsubstituted perbenzoate radical. The likelihood exists that this identity is spurious since the experimental error in the measurement of the benzaldehyde–anisaldehyde system is large and duplicate sets of experiments gave poor checks. Disregarding this anomaly, it further appears that, as might be anticipated, in general, the selectivity and therefore the magnitude of the polar effect increases with the introduction of electron accepting groups in the attacking radical.

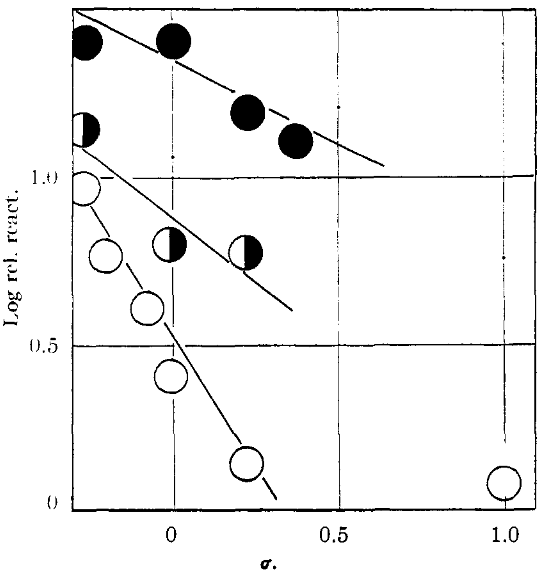


Fig. 2.—Hammett σ values for substituents of substituted benzaldehydes *vs.* log relative reactivities toward 3 perbenzoate radicals: open circles, *p*-chloro-; half shaded, *p*-methoxy; shaded, unsubstituted.

Although oxidations occasionally showed induction periods and shaking rates were neither strictly reproducible nor sufficient to maintain saturation of the reaction mixtures, some qualitative conclusions can be drawn from the oxidation times listed in Table I. Thus, for most pairs, mixtures rich in the more reactive aldehyde oxidized most rapidly, as might be expected if radical concentrations and radical reactivities were roughly constant. However, the reverse is true for *m*-tolualdehyde–*p*-chlorobenzaldehyde, and all systems containing anisaldehyde oxidized slowly, the rate decreasing with increasing anisaldehyde concentrations. Further, in addition to the systems of Table I, several pairs, *p*-chlorobenzaldehyde–*m*-nitrobenzaldehyde, *p*-dimethylaminobenzaldehyde–anisaldehyde, *m*-methoxybenzaldehyde–*p*-chlorobenzaldehyde, and *p*-methylmercaptobenzaldehyde–*p*-chlorobenzaldehyde, were studied which failed to oxidize appreciably in several hours, the last two even in the presence of light and azobis-isobutyronitrile as a photosensitizer. For these exceptional pairs it seems likely that a substituent is susceptible to radical attack, to yield an unreactive radical unable to propagate the chain, and, in partial support of this, it was noted that one ml. of phenylmethyl sulfide reduced the oxidation rate of benzaldehyde in our apparatus at least 500-fold. The susceptibility of –O–C–H and C_6H_5–C–H linkages to radical attack is well established, and the inhibiting effect of nitro compounds in many radical reactions is, of course, well known.

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