recrystallization from ether-petroleum ether afforded a pure sample, m.p. 146.5–147°, $\lambda_{\max}^{CS_2}$ 5.78, 5.88 μ. Mixed melting points with IVc and VIc were depressed to 115–131° and 116–119°, respectively.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.97; H, 8.39. Found: C, C, 65.24; H, 8.26.

Acyloin condensation of diester VIb. A solution of 500 mg. of *cis*-diester (VIb) in 65 ml. of anhydrous ether was added slowly, with simultaneous addition of small portions of sodium, to a mixture of 80 ml. of sodium-dried, distilled liquid ammonia, and 65 ml. of anhydrous ether. The sodium was added at a rate sufficient to maintain a blue color in the solution. Four equivalents of sodium were employed, and the addition was carried out over a period of 2 hr.

The ammonia was then evaporated under a rapid flow of nitrogen. Ether was added along with 2 ml. of methanol, introduced to destroy any residual sodium. The mixture was finally acidified with dilute hydrochloric acid, and the ether layer was washed with water and sodium bicarbonate solution. After drying and evaporation of the solvent the dark, oily product (420 mg.) was chromatographed on alumina. Recrystallization of appropriate chromatographic fractions from ether–petroleum ether afforded 30 mg. of the acyloin (VII), m.p. 77–78°, $\lambda_{\max}^{CS_2}$ 2.80, 5.77 μ, which gave a positive Tollens test.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.07; H, 9.44.

In addition a second product, 53 mg., m.p. 69–70°, was isolated which showed hydroxyl absorption in the infrared at 2.85 μ, but no absorption in the carbonyl region.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18; for $C_{24}H_{38}O_3$: C, 80.39; H, 10.68. Found: C, 80.33; H, 11.23.

The latter compound was not encountered in other experiments in which similar yields of acyloin were produced accompanied by small and variable amounts of *cis*-diester (VIb) and *trans*-diester (IVb).

Degradation of acyloin (VII). A solution of 27 mg. of acyloin (VII) in 1 ml. of 90% acetic acid was treated with 125 mg. of lead tetraacetate in 2 ml. of 90% acetic acid. The mixture was allowed to stand at room temperature for 3 hr., and was then diluted with water and extracted with ether. After thorough washing with water, the ether solution was filtered through anhydrous magnesium sulfate and concentrated to dryness. The residual oil (22 mg.) was esterified directly with diazomethane to give 23 mg. of crude aldehydo-ester, $\lambda_{\max}^{CS_2}$ 3.70 μ. The carbonyl absorption was broad and unresolved.

Oxidation of the latter material was carried out with 20 mg. of chromium trioxide in 2.5 ml. of acetic acid containing a few drops of water. Repeated crystallization of the acidic product (20 mg.) afforded a pure sample (6 mg.) of half-ester VId, m.p. 145–146°; mixed m.p. with *trans* half-ester IVc, 113–123°, with *cis* half-ester VIc, 112–128°, with an authentic specimen of VId, undepressed. The identity of VId obtained by degradation of VII was further established by comparison of the relevant infrared spectra.

HOUSTON, TEX.

[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, THE FACULTY OF ENGINEERING, KYOTO UNIVERSITY]

The Mechanism of the Baeyer-Villiger Reaction of Benzaldehydes with Peroxybenzoic Acid

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The peroxybenzoic acid (PBA) oxidation of benzaldehyde and substituted benzaldehydes in benzene giving corresponding benzoic acids and/or phenols has been studied kinetically; the reaction products have been analyzed by means of gravimetry and spectrophotometry. The rate equation was found to be $v = k_2[\text{ArCHO}][\text{PBA}] + k_i[\text{ArCHO}]^m[\text{PBA}]^n$, where the second term expresses the induced decomposition of the intermediary peroxide adduct. The rate constant k_2 increased by the introduction of electron-attracting groups as well as electron-releasing groups. The induced decomposition was remarkable in *p*- and *m*-nitrobenzaldehydes, especially at high temperature. A mechanism involving a polar radical rearrangement is postulated and discussed.

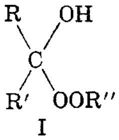
The reactions of carbonyl compounds with peroxy acids, the Baeyer-Villiger reaction,[1] give esters or lactones and, in aqueous media, their hydrolysis products—*e.g.*, alcohols or phenols and carboxylic acids. Two courses, 1a and 1b, are possible for the introduction of oxygen atom.

$$\text{R—CO—R}' + \text{peroxy acid} \begin{array}{l} \nearrow \text{R—CO—OR}' \;(\longrightarrow \text{R—CO}_2\text{H} + \text{R}'\text{OH}) \quad (1a) \\ \searrow \text{R—O—CO—R}' \;(\longrightarrow \text{R—OH} + \text{R}'\text{CO}_2\text{H}) \quad (1b) \end{array}$$

Correspondingly, aldehydes give carboxylic acids or formates and their hydrolysis products.

$$\text{R—CHO} + \text{peroxy acid} \begin{array}{l} \nearrow \text{R—CO}_2\text{H} \quad (2a) \\ \searrow \text{R—O—CHO} \;(\longrightarrow \text{R—OH} + \text{HCO}_2\text{H}) \quad (2b) \end{array}$$

The mechanism involving the formation of an addition compound of peroxyacid I[1-3] or its conjugate acid[3] and the rearrangement of I to products has been postulated because of the isolation of the intermediate and ascertainment of its rearrangement.[4] It has been reported that the addition step is rate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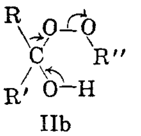
IIb

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[1] (a) A. Baeyer and V. Villiger, *Ber.*, **32**, 3625 (1899). (b) C. H. Hassall, *Org. Reactions*, **9**, 73 (1957). (c) Ya. K. Syrkin and I. I. Moiseev, *Prog. Chem. U.S.S.R.*, **29**, 425 (1960).

[2] *E.g.*, R. Criegee, *Ann.*, **560**, 127 (1948).

[3] Y. Ogata and I. Tabushi, *Bull. Chem. Soc. Japan*, **32**, 108 (1959).

[4] For the example of undecanal, see E. Späth, M. Pailer, and M. Schmid, *Ber.*, **74**, 1552 (1941).

determining for the reactions of acetophenones with peroxybenzoic acid (PBA)[5] and for those of benzaldehydes with peroxyacetic acid,[3] while the rearrangement is rate determining for those of ketones with trifluoroperoxyacetic acid.[6]

The rearrangement has been assumed to involve no radical intermediate[7] but an intermediary cation $RR'C(OH)O^+$ (IIa)[2] or a simultaneous carbanion migration to cationic oxygen atom[8] (IIb), since the reaction is acid catalyzed, and electron-releasing groups accelerate the rearrangement.[1,6] In general, the carbanion rearrangement should be facilitated by the electron-releasing groups as observed in the pinacol rearrangement,[9] but the products, as reported previously, do not completely agree with this prediction. In this article, the peroxybenzoic acid oxidation of substituted benzaldehydes in benzene was studied to confirm the reaction products by means of gravimetry and ultraviolet spectrophotometry and to learn the substituent effect by means of kinetics; the reaction mechanism was discussed on these bases.

EXPERIMENTAL

Materials. Benzaldehydes were purified by fractional distillations (under nitrogen stream) or recrystallizations until their boiling points (liquid) or melting points (solid) agreed with those of literature. Peroxybenzoic acid was prepared from benzoyl peroxide[10] as a solution in benzene and dried with anhydrous sodium sulfate. Benzene was purified by the treatment with concentrated sulfuric acid and then with sodium.

Reaction products. A benzene solution of peroxybenzoic acid (peroxybenzoic acid content was estimated by iodometry and the benzoic acid content by acidimetry) and aldehyde in molar ratio to *ca.* 1.2:1 were mixed in a brown flask and allowed to stand at room temperature in a nitrogen atmosphere until the peroxide disappeared (using the iodide-starch test). An aqueous solution of excess sodium hydroxide was added and benzene was distilled. By this procedure the formate was hydrolyzed. The resulting alkaline solution was added to concentrated aqueous hydrochloric acid to precipitate the carboxylic acids (derived from aldehyde and peroxybenzoic acid); the precipitate was filtered through a glass funnel,[11] dried and weighed.[12] The filtrate containing phenols, formic acid, benzoic acids (substituted) derived from aldehydes, and benzoic acid derived from peroxybenzoic acid was diluted and the contents were analyzed by spectrophotometry using ultraviolet absorption data of standard samples. The filtrate was assumed to be saturated with benzoic acid. Table I shows an example of this analysis.

TABLE I

Starting material	
p-Hydroxybenzaldehyde, 2.442 g.	(0.020 mole)
Benzene solution of PBA ($0.384M$), 65 ml.	(0.025 mole)
Products:	
Precipitate, 3.031 g.	
Dissolved benzoic acid, 0.220 g.[a]	(0.00180 mole)
Precipitated benzoic acid, 0.0250–0.0018 = 0.0232 mole	(2.821 g.)
Precipitated *p*-hydroxybenzoic acid, 3.031–2.821 = 0.210 g.	
Dissolved *p*-hydroxybenzoic acid, 0.436 g.[b]	
Total amount of *p*-hydroxybenzoic acid, 0.646 g.	0.00418 mole (20.9%)
Hydroquinone[c]	0.0148 mole (74.0%)
Corrected ratio of products:	
Hydroquinone, 78%	
p-Hydroxybenzoic acid, 22%	

[a] Based on solubility data,[13] 0.3394 g./100 g. of water. [b] Based on solubility data,[14] 0.0622 g./100 g. of water. Both solutes could not be determined accurately by spectrophotometry because of low concentrations. [c] Based on the following spectrophotometric data: sample, 10^3 dilution of original solution (200 ml.); wave length, 220 mμ, 240 mμ, 280 mμ; optical density, 0.377, 0.100, 0.149.

Though the practical solubilities of benzoic acids under the experimental conditions may be somewhat different from that in pure water, the differences in solubilities do not seriously influence the results, because the amounts of the dissolved acids are much smaller than the precipitated acids plus the dissolved phenols. In addition, the dissolved benzoic acids scarcely disturb the determination of phenols, which can be independently determined by ultraviolet spectrophotometry.

Procedure for rate measurements. A flask, fitted with a gas-inlet tube, a thermometer, an airtight pipet and a reflux condenser with a gas-outlet tube connected to a calcium chloride tube, was used as a reaction vessel. After the flask was filled with nitrogen, a benzene solution of aldehyde was added and thermostated. A thermostated solution of peroxybenzoic acid in benzene was added through the pipet to start the reaction, with continuous introduction of nitrogen gas saturated with benzene. Aliquots were taken out at known intervals of time to determine the remaining peroxybenzoic acid by iodometry.

RESULTS AND DISCUSSION

Products of peroxyacetic acid oxidations of benzaldehydes were benzoic acids and phenols—*i.e.*, the hydrolysis product of formates. The ratio of the phenolic product and the substituted benzoic acid is determined by the migratory aptitude of the aromatic group compared to that of hydrogen. The trend that the benzaldehydes possessing stronger electron-releasing groups give more phenols, while benzaldehyde and those with electron-attracting groups give more benzoic acids,[15] is analogous to other carbanion-migrating rearrangements. Hence, the mechanism involving II seems to be supported in these limited examples. But D'Ans and Kneip

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[5] S. L. Friess and A. H. Soloway, *J. Am. Chem. Soc.*, **73**, 3968 (1951).

[6] M. F. Hawthorne and W. D. Emmons, *J. Am. Chem. Soc.*, **80**, 6398 (1958).

[7] See ref. 1b, p. 76.

[8] See ref. 1b, p. 75.

[9] For example, see W. E. Bachman and F. H. Moser, *J. Am. Chem. Soc.*, **54**, 1124 (1932).

[10] G. Braun, *Org. Syntheses*, **Coll. Vol. I**, 431 (1948).

[11] The solution was diluted to the extent that phenols dissolved completely in the solution.

[12] The value of the whole amount of the precipitate minus the amount of precipitate obtained in the blank procedure with peroxybenzoic acid alone gave the amount of the benzoic acid from the aldehyde beside that dissolved in the filtrate.

[13] M. Kilpatrick and E. Chase, *J. Am. Chem. Soc.*, **53**, 1734 (1931).

[14] A. Osol and M. Kilpatrick, *J. Am. Chem. Soc.*, **55**, 4441 (1933).

have reported that *p*-methoxybenzaldehyde gave only *p*-methoxybenzoic acid[16] instead of *p*-methoxyphenol on oxidation with peroxyacetic acid. The results of peroxybenzoic acid oxidation of *p*-methoxybenzaldehyde in our hands showed that the main product was *p*-methoxybenzoic acid, although a considerable amount of *p*-methoxyphenol was also obtained. Other aldehydes gave results similar to that of peroxyacetic acid oxidations. (Table II). These product ratios, together with kinetic data described below, can not be explained by the ionic rearrangement.

TABLE II

PRODUCT RATIO OF PEROXYBENZOIC ACID OXIDATION OF BENZALDEHYDES

Substituent on Benzaldehyde	Products Phenol, %	 Benzoic acid, %
p-OH	78	22
p-CH_3O	34	66
p-CH_3	26	74
p-H	4	96
p-H[a]	4	96
p-NO_2	0	100

[a] Benzene saturated with water was used as solvent.

Rate equation and the rate-determining step. In an early stage of the reaction, the value of k increased with time. After this induction period, the rate became proportional to the product of concentrations of peroxybenzoic acid and aldehyde. (Fig. 1).

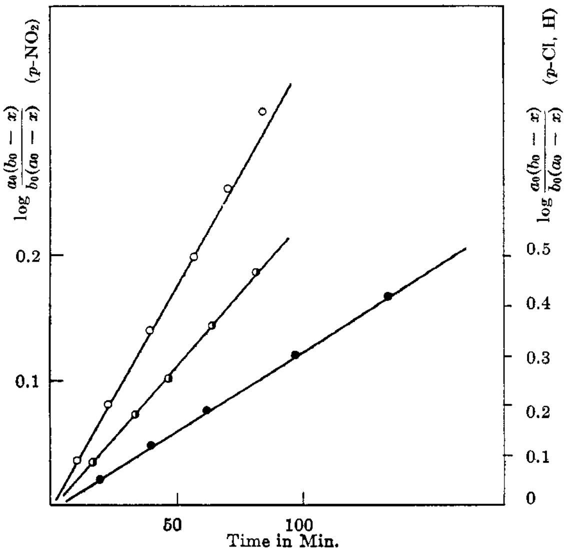
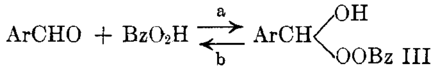


Fig. 1. Typical examples of kinetic runs
-○- *p*-NO_2, 40°
-◑- *p*-Cl, 50°
-●- H, 50°, with 10 vol. % nitrobenzene

Simultaneous determinations of the amounts of peroxybenzoic acid alone and total peroxides in the reaction mixture according to Phillips' method[17] showed that the difference between them was small[18] and that almost all the peroxide was present as peroxybenzoic acid. From these observations it is probable that the rate-determining step is the rearrangement (4) and an intermediate peroxide III is in equilibrium (3) with starting materials, where 3a is not much faster than (4).



$$\text{ArCHO} + \text{BzO}_2\text{H} \underset{b}{\overset{a}{\rightleftarrows}} \text{ArCH}\begin{matrix}\text{OH} \\ \text{OOBz}\end{matrix} \quad \text{III} \qquad (3)$$

$$\text{III} \longrightarrow \begin{cases}\text{ArOCHO} + \text{BzOH} \\ \text{ArCO}_2\text{H} + \text{BzOH}\end{cases} \qquad (4)$$

When III reaches a steady-state concentration, the rate can be expressed as

$$v = k[\text{ArCHO}][\text{PBA}] \qquad (5)$$

The value of k may increase in an early stage until the steady-state is established.

Deviation from eq. 5 was observed with nitrobenzaldehydes at comparatively high conversion.[19] This finding, together with the effect of initial concentrations of reactants described below, shows that the more accurate rate equation may be

$$v = k_2[\text{ArCHO}][\text{PBA}] + k_i[\text{ArCHO}]^m[\text{PBA}]^n \qquad (6)$$

where m and n are nearly equal to 2 and values of k_2 and k_i were shown in Table IV.

Approximate activation energies of bimolecular term (corresponding to k_2) are: *p*-CH_3O, 8.9; *p*-CH_3, 10.6; none, 11.0; *p*-Cl, 7.5; *m*-NO_2, 7.2. (in kcal./mole, average values calculated from extrapolated k_0)

The smaller value of this activation energy compared with that of the decomposition of other peroxides—*e.g.*, activation energies of the decomposition of substituted benzoyl peroxides are[22]; *p*-CH_3O, 28.7, *p*-CH_3, 29.9, unsubstituted, 30.2, *p*-Cl, 30.4—indicates a specific mechanism—*e.g.*, simultaneous formation and fission of bonds—in the reaction. The comparison of these ΔE values with those of other peroxybenzoic acid oxidations is not adequate, as the kind of forming (or breaking) bond of substrate is different. For the discussion of the reaction mechanism, comparison in ΔE's for the decompositions of peroxides is more often recommended.

Effects of initial concentrations of reactants and added materials. The k value varies with initial concentrations of aldehydes and peroxybenzoic acid (Table III and IV). This variation in k is not appre-

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[15] For example, *o*-hydroxybenzaldehyde gave 89% of *o*-hydroxyphenol; *p*-hydroxybenzaldehyde, 93%; *o*-methoxybenzaldehyde, 99%. Also *o*-nitrobenzaldehyde gave 99% of *o*-nitrobenzoic acid; *p*-nitrobenzaldehyde, 90%; *m*-hydroxybenzaldehyde and benzaldehyde, quantitatively. See ref. 1b.

[16] J. D'ans and A. Kneip, *Ber.*, **48**, 1136 (1915).

[17] B. Phillips, F. C. Frostic, Jr., and P. S. Starcher, *J. Am. Chem. Soc.*, **79**, 5982 (1957).

[18] The application of this method, however, could not give accurate results in this case because of the reaction of peroxybenzoic acid with the aldehyde and the self-decomposition of peroxides during the procedure.

[19] As the conversion was relatively low to avoid benzoic acid catalysis, this deviation was not serious except in *p*-nitrobenzaldehyde.

ciable in *p*-methoxy- and *p*-methylbenzaldehydes[19a] but it becomes remarkable in *p*-nitrobenzaldehyde, especially at higher temperature. The extrapolated value of k in the plot of k *vs.* initial concentration of benzaldehyde to zero concentration, k_0, was nearly equal to the k value obtained by adding 1,3,5-trinitrobenzene to stop any radical chain reaction. These observations imply that the change in k may be due to the induced decomposition of peroxide III which corresponds to the second term in Equation 6.

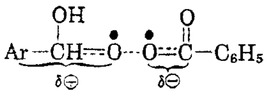
An increase of induced decomposition with electron-attracting substituents was also observed with benzoyl peroxide.[20,21] This increase may be due to (*i*) the decrease in inhibitory action of phenol derivatives substituted with electron-attracting groups and (*ii*) the increased radical nature of the transition state, as both groups attached to O—O linkage are electron attracting. The liberation of free radical was suggested by the oxygen absorption during the reaction (preliminary test). The addition of *m*-dinitrobenzene, instead of difficultly soluble 1,3,5-trinitrobenzene, resulted in inhibition, but k decreased to a value even smaller than k_0 with an increase of concentration of dinitrobenzene. This fact may be due to a kind of medium effect, which was confirmed by the addition of nitrobenzene, a poor inhibitor (see Table III.) On the other hand, addition of benzoic acid increased k owing to the acid catalysis. All these facts are explicable by assuming a transition state with a migrating polar radical like IV which may lead to products in a solvent cage corresponding to the k_2 term, or may liberate free radicals out of the cage corresponding to k_1 term.

TABLE III

EFFECTS OF INITIAL CONCENTRATIONS OF REACTANTS AND ADDED MATERIALS (40 ± 0.1°, IN BENZENE)

Initial Concentrations of Reactants (M) ArCHO	PBA	Added Materials (M)	$k \times 10^4$ (l. mole^{-1} sec.$^{-1}$)
0.1432	0.0620	None	2.79
0.2350	0.0602		2.98
0.2860	0.0573		3.14
0.7080	0.0597		3.72
1.416	0.0575		4.49
0.2348	0.0122		2.04
0.2361	0.0312		2.67
0.2338	0.1112		3.41
0.1880	0.0985		3.30
0.3051	0.0601	BzOH, 0.205	4.07
0.2340	0.0575	BzOH, 0.410	5.85
0.2359	0.0631	None	6.16[a]
0.2383	0.0609	NB,[b] 10 vol. %	5.43
0.2340	0.0595	NB, 25 vol. %	5.12
0.2359	0.0606	NB, 50 vol. %	4.93
0.2379	0.0599	DNB,[c] 0.0148	5.80
0.2365	0.0592	DNB, 0.0296	5.52
0.2398	0.0588	DNB, 0.0592	4.93
0.4719	0.0558	TNB,[d] 0.00705	5.51

[a] Data at 50°. [b] Nitrobenzene was added. [c] *m*-Dinitrobenzene was added. [d] 1,3,5-Trinitrobenzene was added.



$$\mathrm{Ar}\underbrace{-\overset{\overset{\mathrm{OH}}{|}}{\mathrm{CH}}\overset{}{=\!=}\dot{\mathrm{O}}}_{\delta\ominus}\cdots\underbrace{\dot{\mathrm{O}}\overset{}{=\!=}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}}_{\delta\ominus}-\mathrm{C_6H_5}$$

IV

Substituent effect. The product ratios show that hydrogen migrates more easily than would be expected from the ionic mechanism, although electron-releasing groups increase the migratory aptitude of an aryl group, suggesting the polar character of the activated complex. The substituent effects on k_2 do not satisfy the Hammett equation (Table IV), an increase of k_2 being observed with electron-releasing groups and also with strong electron-attracting groups like p-NO$_2$. This behavior is similar to that observed with the first-order radical decomposition of substituted benzoyl peroxides in acetophenone,[22] which has been interpreted in terms of the polar character of dissociating oxygen atoms.[22,23] Thus the observed substituent effects in the benzaldehydes support the polar radical mechanism. An increase of k_2 with electron-releasing substituents may be due to an increase of anionoid character of the migrating group, which facilitates the rearrangement. On the other hand, an increase of k_2 with strongly electron-attracting substituents may be interpreted as the increased radical character of the migrating group[24]; thus hydrogen migration prevails over the aryl rearrangement.

The rate of decomposition of benzoyl peroxide has been expressed as

$$v = k_1[\mathrm{BPO}] + k_i[\mathrm{BPO}]^i \qquad (7)$$

where the second term corresponds to the induced decomposition. Since the concentration of III is proportional to [benzaldehyde][PBA], equations 6 and 7 have the similar forms and give additional support to the mechanism.

Products and radical nature of the reaction. As cited above, benzaldehydes with strongly electron-attracting substituents seem to give a less polar transition state, leading to the product without aryl rearrangement. It was reported that the free

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(19) (a) A small decrease in k was observed with an increase in the initial concentration of *p*-methoxybenzaldehyde. Similar behavior was also observed in the decomposition of substituted benzoyl peroxides[21] (for *p,p'*-dimethoxybenzoyl peroxide and *p,p'*-dimethylbenzoyl peroxide). This phenomenon is still unexplicable, but may be attributed to a kind of inhibition of the radical reaction due to the ring having an electron-releasing group.

(20) W. Cooper, *J. Chem. Soc.*, 2408 (1952).

(21) C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950).

(22) A. T. Blomquist and A. J. Buselli, *J. Am. Chem. Soc.*, **73**, 3883 (1951).

(23) J. Furukawa, *Kagaku*, **8**, 615 (1953).

(24) The initial state becomes unstable by the repulsion of positive charge on both oxygen atoms, and the transition state is stabilized by resonance on introduction of nitro groups.

TABLE IV

k, k_2 AND k_t FOR SUBSTITUTED BENZALDEHYDES

(A) The k value (l. mole^{-1} sec.$^{-1}$)

Substituent	$k \times 10^4$ (30 ± 0.1°)	b_0[a] (*M*)	a_0[b] (*M*)	$k \times 10^4$ (40 ± 0.1°)	b_0 (*M*)	a_0 (*M*)	$k \times 10^4$ (50 ± 0.1°)	b_0 (*M*)	a_0 (*M*)
p-CH_3O	11.7	0.4440	0.0564	19.2	0.2588	0.0549	29.0	0.1110	0.0603
	11.8	0.2198	0.0580	20.3	0.1282	0.0590			
	11.9	0.1120	0.0567	20.6	0.0735	0.0600			
p-CH_3	—			7.00	0.1253	0.0676	12.4	0.1276	0.0601
				7.19	0.2503	0.0575	11.8	0.2608	0.0574
None	1.86	0.2368	0.0613				5.95	0.1887	0.0952
	1.94	0.4932	0.0573				6.16	0.2359	0.0631
	1.99	0.7055	0.0559		[c]		6.30	0.4719	0.0540
							6.74	0.9445	0.0544
p-Cl	2.06	0.4272	0.0566	2.97	0.1423	0.0592	4.92	0.2137	0.0593
	1.98	0.2136	0.0590	3.36	0.2140	0.0596	5.30	0.3159	0.0564
				3.62	0.4276	0.0564	5.81	0.4263	0.0579
m-NO_2	—			3.67	0.1322	0.0589	5.58	0.1664	0.0615
				3.92	0.3962	0.0591	6.32	0.2318	0.0567
							7.18	0.3318	0.0571
p-NO_2	—			5.68	0.1488	0.0610	9.77	0.1321	0.0 20
				6.56	0.2177	0.0632	13.5	0.1652	0.0588
				7.80	0.2977	0.0642	21.2	0.3004	0.0569

(B) Calculated values of k_2 and k_t from the data (A) at 40 ± 0.1°

Substituent	$k_2 \times 10^4$ (l. mole^{-1} sec.$^{-1}$)	$k_t \times 10^4$ (l.^{2} mole^{-2} sec.$^{-1}$)
p-CH_3O	21.0	0
p-CH_3	7.0	0
None	2.6	0.3
p-Cl	2.8	1.7
m-NO_2	3.0	1.9
p-NO_2	3.8	13.4

[a] b_0 is the initial concentration of benzaldehydes. [b] a_0 is the initial concentration of peroxybenzoic acid. [c] Listed in Table II.

radical, (*p*-$CH_3OC_6H_4$)(C_6H_5)$CHCH_2\cdot$, derived from the decarbonylation of the corresponding aldehyde, gave the unrearranged product, (*p*-$CH_3OC_6H_4$)(C_6H_5)$CHCH_3$, while the radical $(C_6H_5)_3CCH_2\cdot$ without a hydrogen atom on α-carbon gave the rearranged product, $(C_6H_5)_2CH\text{-}CH_2C_6H_5$.[25] This finding supports the idea that hydrogen abstraction and migration are easier than the aryl migration in this kind of radical reaction.

The autoxidation of benzaldehydes involves formation of a peroxy radical V,[26] which might be supposed to form peroxide VI and to lead to rearrangement products; but actually no phenol has been isolated in most cases.[27] This phenomenon may be related to the fact that both aryl groups in VI are the same, thus effecting the homolytic fission of the central O—O bond rather than heterolysis.

$$\mathrm{ArCHO} \xrightarrow{\mathrm{R}\cdot} \mathrm{Ar\dot{C}O} \xrightarrow{\mathrm{O_2}} \underset{\mathrm{V}}{\mathrm{ArCOOO\cdot}} \xrightarrow{\mathrm{RH}}$$

$$\mathrm{ArCO_3H} \xrightarrow{\mathrm{ArCHO}} \underset{\mathrm{VI}}{\mathrm{ArCO{-}OO{-}CH(OH)Ar}}$$

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[25] D. Y. Curtin and M. J. Hurwitz, *J. Am. Chem. Soc.*, **74**, 5381 (1952). See also, D. Y. Curtin and J. C. Kauer, *J. Org. Chem.*, **25**, 880 (1960).

[26] For example, see J. R. McNesby and C. A. Hetter, Jr., *Chem. Revs.*, 54, 325 (1954).

[27] Only a small amount of phenol was isolated in some cases; *e.g.*, M. Brunner, *Helv. Chim. Acta*, **10**, 720 (1927).