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Substituent Effect in *o*-Nitroperbenzoic Acid Oxidation of *m*- and *p*-Substituted Acetophenones

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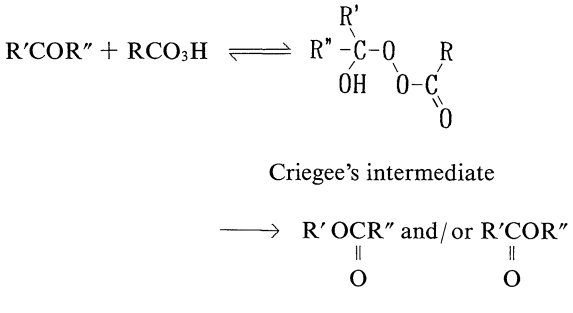
The Baeyer–Villiger reaction of *m*- and *p*-substituted acetophenones (substituents: H, *p*-MeO, *p*-*t*-Bu, *p*-*i*-Pr, *p*-Et, *p*-Me, *p*-Cl, *p*-Br, *m*-MeO, *m*-Me, *m*-Cl) with *o*-nitroperbenzoic acid was studied in chloroform at 30 °C. The rate constants for the general acid catalysis were measured at several concentrations of *o*-nitrobenzoic acid which acted as an acid catalyst. The uncatalyzed and acid-catalyzed rate constants obtained afforded ρ values of −2.16 and −4.11 with σ, respectively. The results indicated that the rate-determining step is the migration of the phenyl group in the peroxy acid-carbonyl adduct for all the substituents studied, whether the reaction is acid-catalyzed or not, and that the acid catalyst intervenes only in the formation of the acid-ketone adduct in the initial state and not in the migration step. The variation of the leaving group abilities required the variation of the substituent constants applied, whereas the acid intervention in the addition step was reflected only in the variation of the ρ value, not in the substituent constants to be applied. The smaller resonance demand for *o*-nitroperbenzoic acid indicated that the structure of the transition state in the migration step was looser and that the position of the transition state was earlier than those for *m*-chloroperbenzoic acid.

It is generally accepted that the Baeyer–Villiger reaction[1a-d] is subject to general acid catalysis and the rate-determining step is the migration in the peroxy acid-carbonyl adduct[2] as depicted in Scheme 1, although



Scheme 1.

there is a possibility that the addition step is rate-determing if the migrating group has a strong electron-releasing moiety.[3] The substituent effect on the Baeyer–Villiger reaction has been studied by many investigators, although reliable data are few because of small numbers of data sets with large experimental errors. Most studies have been done either under conditions where an uncatalyzed "spontaneous" process prevails or under conditions where an acid-catalyzed process prevails. The uncatalyzed reaction of *p*-substituted acetophenones with *m*-chloroperbenzoic acid in chloroform has afforded a ρ value of −1.36 with σ^+,[4] while the acid-catalyzed reactions of *m*- and *p*-substituted acetophenones with trifluoroperacetic acid in the presence of trifluoroacetic acid in ethylene chloride and in acetonitrile have afforded ρ values of −1.10 and −1.45 with σ, respectively.[2] This implies that the substituent constant employed as well as the magnitude of the reaction constant obtained vary with the peroxy acid employed and with the reaction conditions employed, although both reaction systems seem to accompany the other suppressed process to some extent. As to the above acid-catalyzed reaction, the measurements of UV spectra have clearly indicated the presence of a complex of trifluoroacetic acid with acetophenone in ethylene chloride,[2] implying the intervention of the catalyst in the addition step, but no evidence was obtained about whether the migration step is also acid-catalyzed. If the migration step proceeds by a concerted mechanism between the migrating group and the leaving group, the variation of the leaving group abilities is expected to cause some variations in the parameters. Comparisons between the parameters for both processes may give information about whether the catalyst operates in the migration step or not. A similar line of argument is applicable to the addition step. Thus, a correct interpretation of the difference between the parameters is only possible by eliminating the differences in experimental conditions except for the catalyst. With the above goals in mind, we studied the reaction of *o*-nitroperbenzoic acid with *m*- and *p*-substituted acetophenones in chloroform under conditions where both the uncatalyzed and the acid-catalyzed processes proceeded simultaneously.

Results and Discussion

Determination of the Kinetic Law. In order to obtain the kinetic law, an equimolar (5×10^{-2} M) (1 M= 1 mol dm^{-3}) reaction of *p*-methylacetophenone with *o*-nitroperbenzoic acid in chloroform at 30 °C was carried out as a typical example. It was followed by iodometric titration of the residual peroxy acid. Even when the reaction was allowed to start without the acid catalyst, the reaction did not follow any definite kinetic law due to autocatalysis. However, when a certain amount of *o*-nitrobenzoic acid, e.g., 1.5×10^{-2} M, was initially present in the above chloroform solution, the reaction proceeded with an adequate rate and the initial reaction rate strictly

obeyed first-order kinetics (corr coeff: more than 0.999) with respect to the ketone or the peroxy acid concentration to ca. 30% completion of the reaction, although the reaction conditions did not satisfy those of pseudo-first-order kinetics:

$$v = k_{obs}[K], \quad (1)$$

where [K] is the ketone concentration.[5] The influence of the product ester on the reaction rate was not observed at least to 20% completion of the reaction.[6] Equation 1 was followed over the initial ketone concentrations from 2×10^{-2} M to 1.5×10^{-1} M with the invariable observed rate constant so far as the initial concentrations of the other two reactants remained unaltered. To elucidate the apparent simplicity of the kinetics in spite of a lack of pseudo-first-order conditions, it was necessary to examine the relationships between the observed rate constant and the concentration of the other two reactants. The observed rate constant was proportional to the initial peroxy acid concentration over a range of 2.5×10^{-2} to 7.5×10^{-2} M, with the initial concentration of the ketone and the acid kept at 5×10^{-2} and 1.5×10^{-2} M, respectively:

$$k_{obs} = k'_{obs}[PA]_0, \quad (2)$$

where $[PA]_0$ is the initial peroxy acid concentration and k'_{obs} is a constant that depends on the initial acid concentration. With increasing concentrations of the initial acid catalyst over a range of 7.5×10^{-4} to 2.4×10^{-2} M, the value of $k_{obs}/[PA]_0$ linearly increased as shown in Fig. 1, and was expressed as Eq. 3:

$$k_{obs}/[PA]_0 = k_0 + k_{HA}[HA]_0, \quad (3)$$

where $[HA]_0$ is the initial acid concentration, and k_0 and k_{HA} are the rate constants for the uncatalyzed and the acid-catalyzed processes, respectively. The values of these constants were evaluated from the intercept and slope, respectively, by plotting $k_{obs}/[PA]_0$ against $[HA]_0$. The reproducibility of the k_{obs} value was within ±2% on repeated runs, and was considered to be sufficient to calculate k_0 and k_{HA} values. The values obtained are summarized in Table 1. Hammett plots for k_0 and k_{HA} are shown in Figs. 2 and 3, giving ρ values of −2.16 (corr coeff: 0.995) and −4.11 (corr coeff: 0.992) with σ, respectively. Data for *m*-MeO, *p*-Cl, and *p*-Br, which considerably deviated upward from the correlation lines, were not employed for these calculations. Examination of the product(s) by gas chromatography and ^{1}H NMR indicated that the product ester was derived from the exclusive migration of the phenyl group, i.e., *p*-substituted phenyl acetate in *p*-methoxy-, *p*-methyl-, *p*-chloro-, and unsubstituted acetophenones. Another product anticipated from the methyl migration was not detected at all.

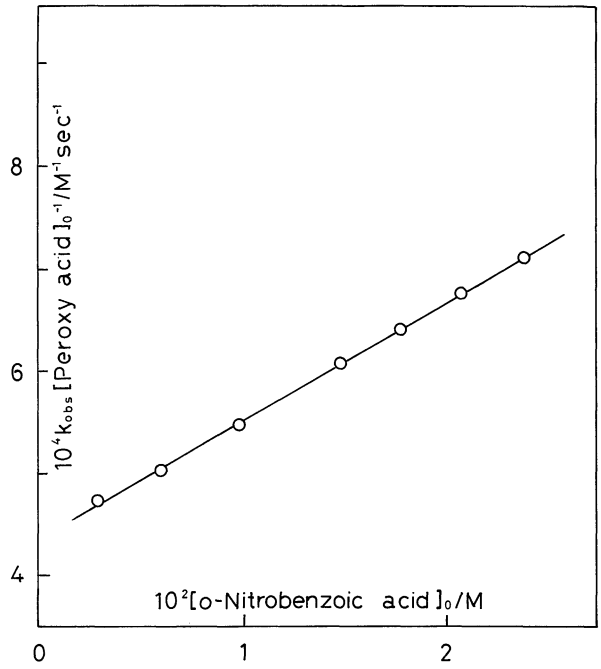


Fig. 1. The plot of $k_{obs}/[PA]_0$ against $[HA]_0$ for *p*-methylacetophenone.

Table 1. k_0 and k_{HA} Values for *o*-Nitroperbenzoic Acid Oxidation of *m*- and *p*-Substituted Acetophenones in Chloroform at 30°C

Substituent	$10^4 k_0/M^{-1} s^{-1}$	$10^3 k_{HA}/M^{-2} s^{-1}$
H	1.79±0.02	1.99±0.02
p-MeO	7.19±0.08	26.1±0.3
p-*t*-Bu	4.84±0.02	13.8±0.1
p-*i*-Pr	4.73±0.02	14.5±0.1
p-Et	4.69±0.01	13.4±0.03
p-Me	4.34±0.05	11.4±0.1
p-Cl	1.10±0.01	0.752±0.003
p-Br	1.05±0.01	0.654±0.004
m-MeO	2.91±0.04	4.43±0.06
m-Me	3.16±0.01	6.92±0.02
m-Cl	0.311±0.001	0.0723±0.0002

Rate-Determining Step and Dependence of Substituent Constant on the Leaving Group. The ρ values obtained in the two plots (see Figs. 2 and 3) were negative, indicating that the migration step played a decisive role for the overall energy of the reaction and therefore was rate-determining for both the uncatalyzed (k_0 process) and the acid-catalyzed (k_{HA} process) processes. With reference to Palmer and Fry's work[4] on the ^{14}C-kinetic isotope effect and substituent effect on *m*-chloroperbenzoic acid oxidation of a series of *p*-substituted acetophenones-1′-^{14}C in chloroform, Ogata and Sawaki[3] pointed out that strong electron-releasing substituents such as *p*-MeO changed the rate-determining step from the migration step to the addition step on the grounds that the *p*-MeO showed no kinetic isotope effect and a downward deviation by ca. 0.5 log unit[7] in Hammett

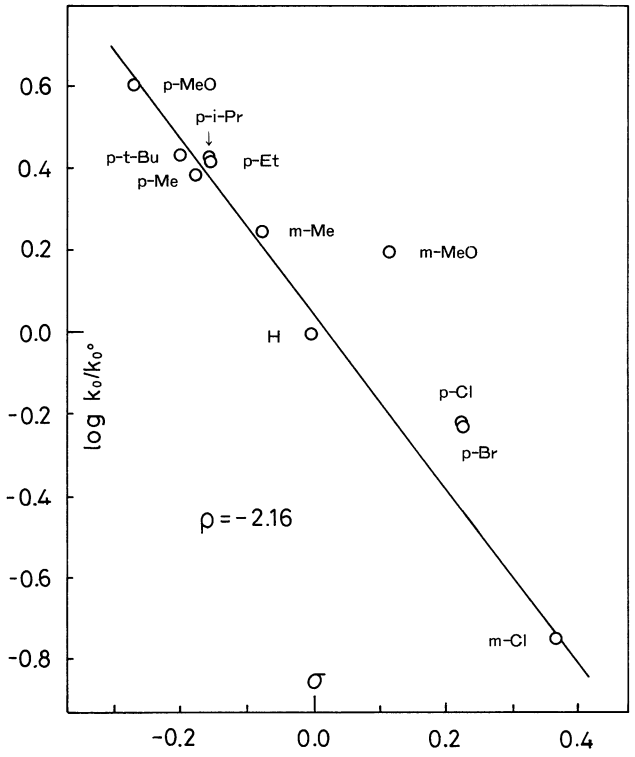


Fig. 2. Hammett plot for the k_0 process.

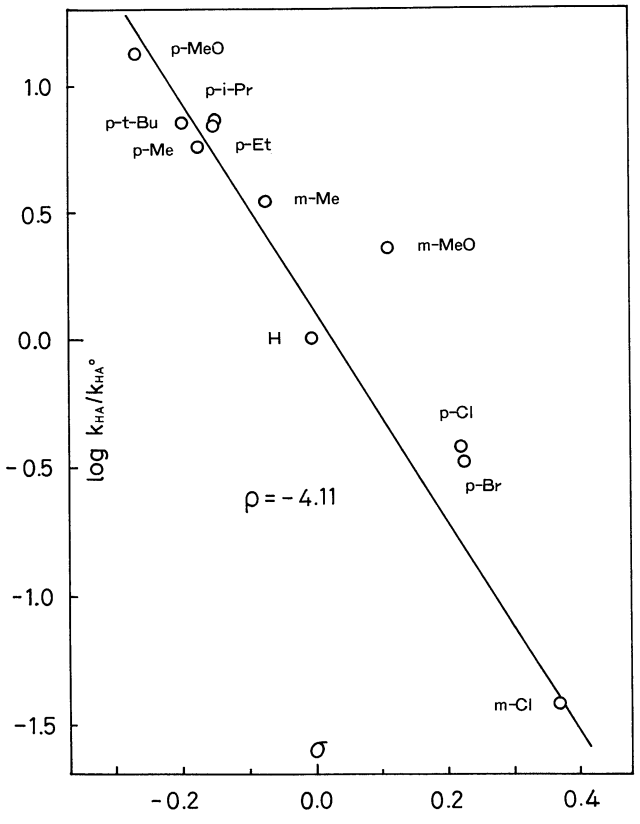


Fig. 3. Hammett plot for the k_{HA} process.

plots with σ^+. The substituent on the peroxy acid may have had little effect on the addition step, because the attack of the peroxy acid on the carbonyl carbon of the acetophenone occurs at its terminal oxygen conjugatively insulated from the rest of the peroxy acid. The substituent on the phenyl group of the acetophenone should have a normal effect expected from the ordinary carbonyl addition reactions in this step. On the other hand, in the migration step, the benzoyloxyl group, which originates from part of the peroxy acid, acts as a leaving group. A substituent on the group is expected to influence the reaction, as is described below. The substituent effect due to the migrating phenyl group should largely depend on the degree of the participation of the migrating phenyl on the migration-terminus oxygen. The degree of the phenyl participation, in turn, depends on the ability of the leaving group to depart from the oxygen, as long as the migration proceeds synchronously. As a whole, the difference in the substituent effects observed between the case for *m*-chloroperbenzoic acid and that for *o*-nitroperbenzoic acid is exclusively attributable to the difference in the leaving abilities of the benzoyloxyl groups between the peroxy acids in the migration step, and is not ascribed to the difference in the substituent effects between the peroxy acids in the addition step, since the electrophiles employed were the same for both reaction systems. If the leaving group ability is closely related to the acidity of the carboxylic acid from which the leaving group is derived, the leaving ability of the *m*-chlorobenzoyloxyl group is lower than that of the *o*-nitrobenzoyloxyl group. A better leaving group decreases the energy of the transition state more in the migration step. The rate-determining step in our case was the migration step for all the substituents studied, including the *p*-MeO group. The case for *m*-chloroperbenzoic acid should have been in the same category as that for *o*-nitroperbenzoic acid, since, in the former case, the reaction required more energy of the transition state in the migration step and therefore later transition state[8] and stronger π-interaction between the migrating phenyl π-system and the migration-terminus oxygen than those for *o*-nitroperbenzoic acid. Since the reported rate constants to which the Brown $\rho^+\sigma^+$ equation was applied were of second order (first order in ketone and first order in peroxy acid), it seemed to imply that the reaction had been carried out under the condition $k_0 \gg k_{HA}[HA]$ for *m*-chloroperbenzoic acid. Even if the rate constants observed corresponded to the k_0 values, it was still better to apply the data set to the Yukawa–Tsuno equation than the Brown $\rho^+\sigma^+$ equation used by Palmer and Fry,[4] and by Ogata and Sawaki.[3] The former equation gave a ρ value of -1.62 and a corr coeff of 0.993 when an r value of 0.54 was adopted.[9] Thus, the variation of the leaving group abilities required the variation of the substituent constants applied. The variation of the resonance demand suggested that the structure of the transition

state in the migration step was tighter for *m*-chloroperbenzoic acid than for *o*-nitroperbenzoic acid and therefore the position of the transition state was relatively late for the former, and vice versa. This was in good agreement with theoretical predictions for the transition-state geometry of the Baeyer–Villiger reaction.[10]

Acid Catalysis in the k_{HA} Process. The k_0 process gave a ρ value of -2.16 with σ as a result of opposite substituent effects between the addition step and the migration step. In the k_{HA} process, a ρ value of -4.11 was obtained with σ. The magnitude of the $|\rho|$ value for the k_{HA} process was almost twice as large as that for the k_0 process. This large difference in magnitude could be rationalized by examining the influence of the acid intervention on the individual steps in the k_{HA} process. If the acid catalyst acts only on the carbonyl or acyloxy oxygen of the leaving group in the migration step, the leaving group departs much more easily from the rest of the Criegee's intermediate. The better leaving group induced by the acid catalyst would thus decrease the energy of the transition state more in this step, promoting the earlier transition state and making it more reactant-like,[8] viz., more Criegee's intermediate-like. The substituent effect on the migration step would therefore decrease due to the less effective participation of the phenyl group on the migration-terminus oxygen in the k_{HA} process than that in the k_0 process. Thus, the overall substituent effect on the k_{HA} process was expected to become much smaller in magnitude than that on the k_0 process. The relative magnitude of the observed ρ values, however, showd the reverse, which indicated that the contribution of the acid catalyst to the migration step of the k_{HA} process should have been negligibly small or ruled out. On the other hand, if the acid catalyst operates only on the carbonyl group of the acetophenone in the initial state, the polarization of the carbonyl group is enhanced even by weak hydrogen bonding,[11] making the ketone more reactive to the nucleophile. It has been shown that acid-catalyzed carbonyl addition reactions are relatively insensitive to the substituent effect.[2,12] The acid-catalyzed addition step in this reaction would therefore be facilitated with a smaller contribution of the substituent effect. Consequently, the overall substituent effect would be mainly governed by the substituent effect on the migration step. A larger $|\rho|$ value was expected in the k_{HA} process than in the k_0 process. This was in good accordance with the relative magnitude of the $|\rho|$ values obtained in both processes. Since the substituent effect on the migration step was nearly the same for the k_0 process and the k_{HA} process in this case, the difference (1.95) in the observed ρ values between the two processes should refer to the intervention of the acid catalyst in the addition step of the k_{HA} process. The last possibility is that the acid catalyzes both the addition step and the migration step successively. As discussed above separately, the intervention of the acid catalyst decreases the substituent effect on each step. Neither of the influences of the decreases in the individual steps on the ρ value is therefore predominant, and the decrease in the rate-determining migration step would probably be a little larger than that in the addition step. The ρ value in the k_{HA} process was therefore expected to become one between the ρ values for the two extreme cases mentioned above, and to be comparable to that in the k_0 process. As for the trifluoroperacetic acid oxidation of *m*- and *p*-substituted acetophenones in the presence of trifluoroacetic acid,[2] the acid-catalyzed process seemed to predominte ($k_0 \ll k_{HA}[HA]$). The low nucleophilicity and the low basicity of the leaving group were coincident with the applicability of the σ value. Although the ρ value for the k_0 process was not available for trifluoroperacetic acid, the fact that the magnitude of the ρ value for trifluoroperacetic acid was ca. a third of that for *o*-nitroperbenzoic acid in the k_{HA} process seemed to imply the acid intervention in the migration step as well as in the addition step.

Similarity Between the k_0 Process and the k_{HA} Process. In Fig. 4 the logarithmic rates for the k_{HA} process are plotted against those for the k_0 process, giving a linear correlation with a corr coeff of 0.999 including *m*-MeO, *p*-Cl, and *p*-Br which deviated upward from the lines of Hammett plots (Figs. 2 and 3). This indicated that these two processes proceeded essentially by the same mechanism, although there was pre-equilibrium for the formation of the acid-ketone adduct in the k_{HA} process.

Abnormality for Some Substituents. *m*-Methoxyacetophenone deviated upward from the Hammett lines (Figs. 2 and 3) by ca. 0.4 and 0.7 log unit for the k_0 process and for the k_{HA} process, respectively, while *p*-methoxyacetophenone showed normal behavior on the lines. The basicity of the substituent, *p*-MeO, is decreased due to its conjugation with the carbonyl of the

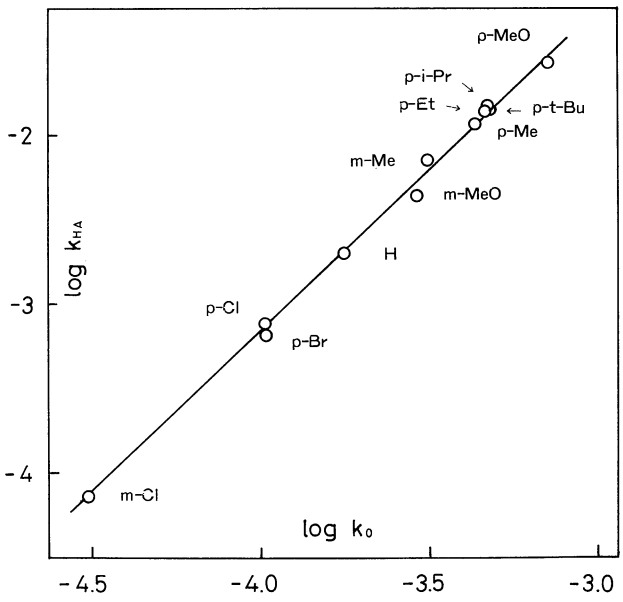


Fig. 4. Linear free energy relationship of k_{HA} vs. k_0.

ketone, whereas *m*-MeO is conjugatively insulated from the carbonyl. It is conceivable that *m*-MeO maintains its basicity enough to form a hydrogen bond with the solvent (specific solvation effect) in the initial state, making the substituent more electron-attractive and therefore making the ketone more reactive in the addition step. Similar enhancement has been observed for *m*-MeO by Friess and Soloway[13] in the reaction of *m*- and *p*-substituted acetophenones with perbenzoic acid in chloroform. The substituents *p*-Cl and *p*-Br also showed upward deviations from the Hammett lines by ca. 0.23—0.24 and 0.34—0.38 log unit for the k_0 process and for the k_{HA} process, respectively. These deviations are a little too large to be regarded as experimental errors. Considering that *m*-Cl behaved well, it might be conceivable that a free radical path (homolytic fission of the –O–O– bond in the Criegee's intermediate)[14] for *p*-Cl and *p*-Br was accompanied in the migration step. The radical reaction may have been accelerated by *p*-halophenyl participation on the migration-terminus oxygen.

Experimental

The boiling points are uncorrected. ^{1}H NMR spectra were obtained on a JEOL JNM-MH 60 spectrometer in δ values relative to the internal TMS. Gas chromatographic analyses were carried out on a Hitachi K 53 with a 30-m golay column of apiezon L high vacuum grease and FID.

***o*-Nitroperbenzoic Acid.** The title compound was prepared by the reaction of *o*-nitrobenzoic acid with 90% hydrogen peroxide in methanesulfonic acid, according to the procedure described by Silbert et al.[15] Further treatment was necessary for its use in the kinetic experiments. The compound obtained was dissolved in purified chloroform at room temperature, washed with distilled water four times in order to remove a trace of methanesulfonic acid, and then dried over anhydrous sodium sulfate for a few minutes. After the sodium sulfate was removed by filtration, the filtrate was concentrated under reduced pressure at 30 °C until a certain amount of the compound had precipitated. This precipitate was redissolved at a temperature not above 40—45 °C within ten minutes. After filtration, the solution was cooled to −20 °C to give light yellow needles. The amount of active oxygen was estimated to be 100±1% by iodometric titration. The compound was kept in a refrigerator.

***p*-Substituted Acetophenones.** *p*-Methyl-, *p*-chloro-, and *p*-bromoacetophenones were prepared by Friedel–Crafts reactions following the usual procedure in carbon disulfide.[16] *p*-Methoxy-, *p*-*t*-butyl-, *p*-isopropyl-, and *p*-ethylacetophenones were prepared by the Perrier modification[17] of the Friedel–Crafts reaction in carbon tetrachloride. The compounds were purified through the recrystallization of their semicarbazones except for *p*-methoxyacetophenones, followed by repeated distillations of regenerated ketones using concd HCl. *p*-Methoxyacetophenone was purified by fractional recrystallization, followed by distillation. Commercially-obtained acetophenone was purified by repeated distillations. The compounds thus obtained were all pure according to gas chromatography. Substituents and boiling points for these compounds were as follows: *p*-MeO, 142.0—142.5 °C/18 mmHg (lit,[18] 139 °C/15 mmHg) (1 mmHg=133.32 Pa); *p*-*t*-Bu, 140—140.5 °C/18 mmHg (lit,[17] 137—138 °C/16 mmHg); *p*-*i*-Pr, 123.0—123.5/14.5 mmHg (lit,[19] 115 °C/10 mmHg); *p*-Et, 127 °C/22 mmHg (lit,[17] 116—117 °C/13 mmHg); *p*-Me, 105 °C/18.5 mmHg (lit,[18] 93.5 °C/7 mmHg); *p*-Cl, 118 °C/20 mmHg (lit,[18] 99.0 °C/7 mmHg); *p*-Br, 133.5—134.0 °C/19.5 mmHg (lit,[18] 117.0 °C/7 mmHg); H, 84.5—85.0 °C/17 mmHg (lit,[18] 88.5 °C/16 mmHg).

***m*-Substituted Acetophenones.** *m*-Methoxy-, *m*-methyl-, and *m*-chloroacetophenones were prepared by the usual procedures from *m*-hydroxyacetophenone, *m*-methylbenzoic acid and *m*-aminoacetophenone, respectively, and were purified by the same manner as described in the preparation of the *p*-substituted acetophenones. The compounds obtained were all pure according to gas chromatography. Substituents and boiling points for these compounds were as follows: *m*-MeO, 132 °C/20 mmHg (lit,[20] 125—126 °C/12 mmHg); *m*-Me, 109 °C/22 mmHg (lit,[21] 65—71 °C/0.2 mmHg); *m*-Cl, 110.5—111.5 °C/17 mmHg (lit,[22] 80 °C/2.5 mmHg).

Solvent. Chloroform used for the kinetics as a solvent was purified by washing with concd sulfuric acid as described in the literature[23] just prior to use.

Product Analyses. The reaction products were analyzed by use of ^{1}H NMR and gas chromatography. The analytical procedures in the case of acetophenone described below were also applied to the other cases of *p*-methoxy-, *p*-methyl-, and *p*-chloroacetophenones. At the end of a kinetic run, the residual solution was examined by ^{1}H NMR, which showed no signal (δ=3.94) for the methyl group of the methyl ester but showed a signal (δ=2.28) for that of the acetate and a signal (δ=2.62) for that of the unreacted ketone. Blank tests proved that the detection of the methyl ester was possible when the molar ratio of methyl ester to acetate was higher than 3/100. Another portion of the residual solution was washed successively with cold 5% potassium iodide aq once, with cold 3% sodium thiosulfate aq twice, with cold 6% sodium hydrogencarbonate aq three times, and finally with cold water twice. After the solution was dried on a small amount of sodium sulfate, the solvent was evaporated under reduced pressure. Gas chromatographic analysis of the liquid residue showed the complete absence of the methyl ester. Blank tests proved that neither the methyl ester nor the acetate was hydrolyzed throughout the above treatment, and that the detection of the methyl ester was possible when the molar ratio of methyl ester to acetate was higher than 1/100, except for *p*-chloroacetophenone where the retention times were the same for the unreacted ketone and the methyl ester. As for the other ketones listed above, the results obtained were similar to those of acetophenone.

Kinetic Measurements. The reaction rates were determined by iodometry of unreacted peroxy acid using the usual ampule technique. In a 100-ml glass-stoppered flask ca. 5×10^{-3} moles of ketone and ca. 1.5×10^{-3} moles of *o*-nitrobenzoic acid were weighed accurately and were dissolved in 50-ml of chloroform. In another 100-ml glass-stoppered flask ca. 5×10^{-3} moles of *o*-nitroperbenzoic acid were weighed accurately and were likewise dissolved in 50-ml of chloroform. After the flasks and the contents were cooled to 0—5 °C in an ice-bath, the *o*-nitroperbenzoic acid solution was added to the solution of the ketone and the acid. The combined solution was swirled quickly and 7—8-ml samples of the solution were sealed in

twelve ampules for each kinetic run. They were immersed into a bath thermostated at 30.00±0.02 °C at the same time. The ampules were withdrawn at adequate intervals and quenched with ice. A 5-ml portion of the solution was pipetted out and transferred into 30-ml of a 2.5% aqueous solution of potassium iodide to which 10-ml of 1 equiv HCl solution had been added immediately before pipetting. The iodine thus liberated was titrated with a 0.1 equiv $Na_2S_2O_3$ solution. All kinetic measurements satisfied the first-order kinetic equation with a correlation coefficient $R>0.999$ to ca. 30% completion of the reaction.

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5) The empirical Eq. 1 can be paraphrased by

$$v = k_{obs}[PA], \quad (1')$$

where [PA] is the peroxy acid concentration. We can not distinguish Eq. 1 from Eq. 1′ in practice, because the behavior of the ketone and the peroxy acid is the same in terms of the stoichiometry.

6) When the reaction was allowed to start with the same initial concentration ratio of each reactant as the composition ratio at 20% completion of the reaction excluding product ester, the reaction-rate constant observed was still the same as the rate constant at the standard conditions employed in this study.

7) Ogata and Sawaki also regarded *p*-CN as an improper substituent because of a possibility of methyl migration for *p*-cyanoacetophenone. Thus, they used three substituents, i.e., H, *p*-Me, and *p*-Cl among five substituents reported by Palmer and Fry to correlate with σ^+. The downward deviation by ca. 0.5 log unit for the *p*-MeO is that from the correlation line.

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9) We included here *p*-CN and *p*-MeO to calculate the correlation line by use of the equation $\log k/k_0=\rho[\sigma+r(\sigma^+-\sigma)]$ for a wider coverage (the notation k_0 in this equation means the rate constant for the unsubstituted compound). There is no distinct evidence for the methyl migration in the case of *p*-cyanoacetophenone.

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