[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Reactions of Peracids. V.[1] The Reaction of Substituted Acetophenones with Perbenzoic Acid[2]

BY S. L. FRIESS AND A. H. SOLOWAY

From the reaction of meta- and para-substituted acetophenones with perbenzoic acid in chloroform solution, the corresponding acetate esters have been obtained in 50–80% yield. The kinetics in chloroform and in mixed solvents for this reaction have also been investigated. The ketones fall into two categories with respect to their kinetic behavior; those ketones substituted by electron-attracting groups in general conform to first order kinetics, while those possessing electron-supplying groups meta or para to the acetyl function exhibit second order kinetics. In the reactions with peracid, acetophenone, as the transition compound, exhibits a mixed order of reaction. Regardless of kinetic order, these reactions are all characterized by unusually high values for $\Delta S\ddagger$. For both types of ketones, (1) a more polar solvent has been found to accelerate the over-all reaction, and (2) catalysis by benzoic and acetic acids has been demonstrated.

Discussion

It has previously been noted[3] that acetophenone reacts with perbenzoic acid in chloroform solution at room temperature to yield the single observed product phenyl acetate

$$C_6H_5COCH_3 + C_6H_5CO_3H \xrightarrow{CHCl_3} C_6H_5OCOCH_3 + C_6H_5CO_2H$$

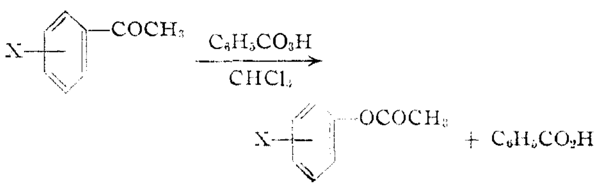
In closely related work using peracetic acid as the oxidant in glacial acetic acid solvent, Doering and Speers[4] found that both isomeric esters corresponding to methyl and phenyl group migration could be obtained from acetophenone.

It has also been observed[1] that a phenyl group conjugated with the carbonyl function markedly lowers the relative rate of reaction with peracid, as compared to the rate found for a saturated alicyclic compound such as cyclohexyl methyl ketone.

Accordingly, it was of particular interest in the present work to study the reaction of substituted acetophenones with perbenzoic acid, both with respect to yields of products and absolute rates of reaction, as a function of systematically varied electron-supplying or attracting groups meta or para to the acetyl function.

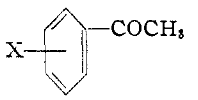
Product Studies.—In preliminary studies on a preparative scale, several representative acetophenones were subjected to the action of excess perbenzoic acid in chloroform solution at room temperature, and the products isolated and identified. The results of these runs are shown in Table I.

As indicated by the data of Table I, a yield of up to 80% of a single ester is obtained from each ketone in the reaction

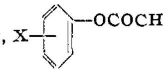


In no case was there evidence for any detectable amount of the isomeric methyl ester resulting from methyl group migration during the course of the reaction.

TABLE I

REACTION OF  WITH PERBENZOIC ACID

Solvent, chloroform; temperature 23–25°

Substituent X	Initial molar ratio (peracid)/(ketone)	Reaction time[c] (hr.)	Ester, X– 			
			Yield,[b] %	B.p., °C.	Mm.	M.p.,[f] °C.
H[a]	1.20	240[d]	63[e]	93–93.5	22	
p-OAc	1.09	500	80			124–125
p-NHAc[g]	1.08	525	80			149.5–151
p-OCH$_3$	2.57	215	66			30–41
p-CH$_3$	1.48	1900	73[h]			44–45[i]
m-OCH$_3$	1.27	480	52[j]			101–102[k]
p-Cl	1.47	504	57[l]			92–93[m]

[a] See reference 1. [b] Based on initial amount of ketone. [c] Time at which product was worked up after complete disappearance of peracid; in most cases the reaction was completed earlier. [d] 0.65 molar equivalent of peracid was consumed by this time. [e] Corrected for all recovered ketone. [f] All melting points were undepressed on admixture with authentic samples of the respective esters. [g] Went into solution slowly as it reacted. [h] Based on weight of dibromocresol isolated after saponification of crude ester. [i] Melting point of the dibromocresol; mixed melting point with authentic sample undepressed. [j] Determined by isolation of the tribromophenol derivative obtained upon saponification of the crude ester. [k] M.p. of the tribromophenol derivative. [l] Yield of the dibromophenol derivative obtained from crude ester. [m] M.p. of the dibromophenol derivative.

Rate Studies.—The formation of a single product in high yield made feasible a detailed study of the kinetics of the general reaction, and in particular a correlation of relative rates of reaction with the nature of the substituents present on the phenyl rings of the reactant ketones. Such a study was initiated on the series of ketones shown in Table II. Here the range of substituents in meta and para positions varied from strongly electron-supplying groups such as methoxyl and methyl, to electron-withdrawing groups such as nitro, the halogens, and the acetoxy group.

In Table II, a graphically-obtained, numerical value for *either* a first order rate constant (k_1) or a second order rate constant (k_2) in chloroform solvent is listed for each compound, depending upon which type of rate formulation best fits its kinetic data. The assignment of first or second order to a given ketone reaction was based on the constancy of either k_1 or k_2 values for runs with varying initial

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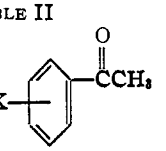
[1] For article IV in this series see: S. L. Friess and N. Farnham, THIS JOURNAL, **72**, 5518 (1950).

[2] Presented in part before the Division of Organic Chemistry, 118th Meeting of the American Chemical Society, Chicago, Illinois, September 3-8, 1950.

[3] S. L. Friess, THIS JOURNAL, **71**, 14 (1949).

[4] W. von E. Doering and L. Speers, *ibid.*, **72**, 5515 (1950).

TABLE II

RATE RUNS ON REACTION OF  WITH $C_6H_5CO_3H$

$X-C_6H_4-COCH_3$

Solvent, chloroform; temperature, 29.90 ± 0.10°

Ketone X =	Batch of peracid	(Ketone)° mole/l.	(Peracid)° mole/l.	k_1 (sec.$^{-1}$) × 10^6	k_2 (l./mole sec.) × 10^5
p-OCH_3	A	0.134–0.229	0.189		4.42 ± 0.10
p-CH_3	B	.137– .235	.149–0.199		3.20 ± .16
m-OCH_3	C	.114– .195	.166		2.42 ± .18
p-Cl	D	.112– .192	.162	2.08 ± 0.09	
p-$OCOCH_3$	E	.097– .136	.122– .162	2.04 ± .09	
p-Br	F	.100– .172	.136– .180	1.95 ± .09	
m-Br	G	.127– .217	.182	1.01 ± .02	
p-NO_2[a]	H	.123– .245	.139– .174	0.23 ± .02	
m-NO_2[a]	I	.130– .223	.186	1.30 ± .09	

[a] None of the expected esters could be isolated from the reaction mixtures of these runs; starting material was recovered.

concentrations of reactants. Representative rate runs for ketones of both types are shown on Fig. 1.

Since each ketone was investigated using a different batch of peracid, and the activity of each peracid solution is known[5] to vary according to the amount of benzoic acid which it contains, it was necessary to run a standard ketone along with each substituted acetophenone so that all rate constant values to be correlated could be normalized to a fixed peracid activity. The standard employed was unsubstituted acetophenone itself, in a 1:1 ratio of initial (peracid):(ketone) for each run.

Accordingly, preliminary studies were made of the kinetics of the reaction of acetophenone with perbenzoic acid in chloroform. It was found that this reaction was neither first nor second order in character. Although a given run analyzes equally well by either of these formulations, runs in which initial concentrations of reactants are varied exhibit no constancy of the calculated k_1 or k_2 values. Empirically, the acetophenone data from a large number of runs at 29.90° using various peracid batches are quite well fitted by the following formulation, in which the observed k_1 values are linearly related to initial ketone concentrations

$$k_1 = (1.51 \pm 0.03)10^{-6} + (0.52 \pm 0.02)(10^{-5})(\text{ketone})$$

In using acetophenone as a standard ketone, at a fixed 1:1 ratio of (ketone):(peracid), its rate constant found in each peracid solution was taken as an index of the activity of that solution. The values for rate constants on unsubstituted acetophenone taken as representative of standard activity were 2.40×10^{-6} sec.$^{-1}$ as an apparent over-all k_1, or 1.58×10^{-5} l./mole sec. as an apparent k_2 value. Accordingly, for those substituted ketones whose kinetics best fit a first order formulation, all k_1 values have been normalized, by use of the standards run with those ketones, to the above average k_1 for acetophenone, and a similar normalization to the above average k_2 value has been made for each ketone of Table II fitting a second order law.

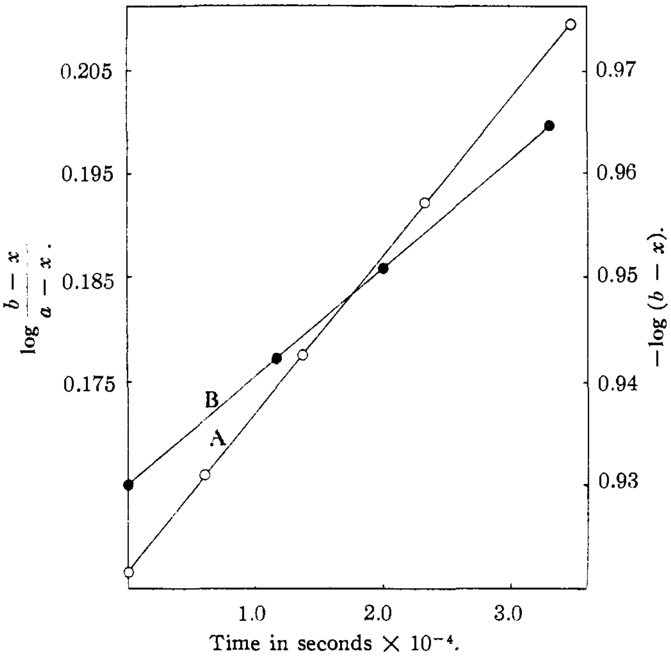


Fig. 1.—A, first-order plot for p-acetoxyacetophenone, $(\text{ketone})_0 = 0.1357$ M, $(\text{peracid})_0 = 0.1217$ M; B, second-order plot for p-methylacetophenone, $(\text{ketone})_0 = 0.1373$ M, $(\text{peracid})_0 = 0.1991$ M; temperature, 29.90°.

Since, as will be shown later, certain of the ketone–peracid reactions are susceptible to acid catalysis, with marked autocatalysis evident at later stages of the reaction, the rate constants of Table II were obtained graphically for approximately the first 20% of the reaction, over which region excellent linearity of plots was observed.

As the data of Table II indicate, the kinetics of the peracid reaction are closely dependent on the type of substitution present in the phenyl ring. Electron-supplying groups meta or para to the acetyl function lead to clear second order kinetics, and produce sensitivity to acid catalysis. In contrast, those ketones whose meta or para ring positions are substituted by electron-attracting substituents exhibit definite first order kinetics, with the magnitude of observed k_1 values approximately independent (except for nitro compounds, from which no ester

[5] S. L. Friess, THIS JOURNAL, 71, 2571 (1949).

product could be isolated) of the substituent present. In these first-order reactions, the majority exhibit some degree of acid catalysis, but no catalysis by benzoic acid was observed for *p*-acetoxyacetophenone.

In addition to the kinetic behavior noted above, the data permit the generalization that, with respect to the effect of substituents on the speed of reaction, electron supply toward the carbonyl increases the rate of reaction with peracid, as compared to the unsubstituted reference compound, while electron withdrawal decreases this rate of reaction.

It is of some interest to note that the reaction of these substituted acetophenones with perbenzoic acid exhibits a relative set of rates which roughly parallels the rates of semicarbazone formation from these ketones, as observed by Cross and Fugassi.[6] Thus for the peracid reaction the relative rates run in the sequence

$$p\text{-OCH}_3 > p\text{-CH}_3 > m\text{-OCH}_3 > \text{H} > p\text{-Cl} > p\text{-OAc} > p\text{-Br} > m\text{-Br}$$

The available sequence on the rate of semicarbazone formation is

$$p\text{-OCH}_3 > p\text{-CH}_3 > \text{H} > p\text{-Cl} > p\text{-Br}.$$

It is perhaps significant to note that in each of these series, the relative rates of reaction in general increase with increasing electron supply[7] by substituents operating from the meta or para positions. The *m*-methoxy group alone falls out of line in the above generalization, since it possesses a positive σ value, and consequently should impart to its ketone a rate of reaction smaller than that of the unsubstituted ketone, whereas actually this rate of reaction is greater.

Another interesting effect appears in the behavior toward peracid of *p*-acetoxyacetophenone. It is observed that the $p\text{-CH}_3\text{COO}$ substituent leads to behavior of its ketone strikingly similar to that afforded by the halogens, *i.e.*, first order kinetics for the ketone reaction and an over-all rate slower than that shown by the unsubstituted acetophenone. From these data it would seem that the acetoxy group exerts the same deactivating influence on an aromatic nucleus as that evidenced by the halogens. Polarographic[8] evidence pointing to the electron-withdrawing nature of the acetoxy group has appeared previously in the literature, and ultraviolet absorption spectrum data on substituted acetophenones[9] also indicate that replacement of the *p*-OH group by *p*-OAc results in complete loss of the electron donor properties associated with the para hydroxyl substituent.

In addition to the ketones whose rates of reaction are reported in Table II, *p*-hydroxyacetophenone was subjected to rate studies under the same conditions as the other members of the series and showed excellent conformity to second order kinetics over a range of reactant concentrations, with an observed k_2 value of $(1.15 \pm 0.01)\ 10^{-4}$ l./mole sec. However it was found that this ketone consumed more than two moles of peracid in the over-all reaction, when permitted to do so, and rapidly developed color during the peroxidation process, pointing to nuclear degradation as the predominant reaction. No acetate product could be obtained from the reaction mixture. This behavior is understandable on the basis of ready oxidation of phenols and naphthols by perbenzoic acid, as recently observed by Fernholz.[10]

Acid Catalysis.—As an illustration of the general effect of added acids on the rates of reaction of several ketones, Table III gives specific data for acetophenone and its $p\text{-CH}_3$ and *p*-Br derivatives. It is observed that benzoic acid markedly accelerates the rate of a second order reaction, whereas the effect of acetic and benzoic acids on the first order type is much less pronounced, but still apparent.

This catalysis by added weak acids mirrors that found in the closely related peracid oxidation of cyclanones.[5]

TABLE III

CATALYSIS OF KETONE–PERACID REACTION

Solvent, chloroform; temperature, 29.90 ± 0.10°

Acetophenone	(Ketone)$_0$ (mole/l.)	(Peracid)$_0$ mole/l.	Added catalyst (C_6H_5COOH)$_0$	Added catalyst (HOAc)$_0$	$k_1^a \times 10^6$ sec.$^{-1}$	$k_2^a \times 10^5$ l./mole sec.
Unsubstituted	0.187	0.186	...	...	2.40	
	.187	.186	...	0.187	3.24	
	.187	.186	0.188	...	3.37	
$p\text{-CH}_3$	.196	.199	...	...		3.23
	.196	.199	.065	...		4.78
p-Br	.143	.136	...	...	1.99	
	.143	.136	.183	...	2.84	

[a] Normalized values.

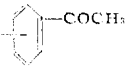
Effect of Solvent on Reaction Rate.—To obtain additional information as to the nature of the fundamental oxidation process, the effect of solvent on the reaction rates of *p*-chloroacetophenone and *p*-methylacetophenone was determined. These ketones were selected as representatives of the classes characterized by first *vs.* second order kinetics.

The solvents employed, in order of increasing polarity, were: (1) chloroform; (2) 40% chloro-

TABLE IV

EFFECT OF SOLVENT ON REACTION RATE

Temperature 29.90 ± 0.10°, (peracid)$_0$/(ketone)$_0$ = 1.0

Ketone 	Solvent	$k_1^a \times 10^6$ (sec.$^{-1}$)	$k_2^a \times 10^5$ (l./mole sec.)
p-Cl	$CHCl_3$	2.08 ± 0.09	
	60% TCE 40% $CHCl_3$	2.36 ± 0.03	
	60% CH_3OH 40% $CHCl_3$	3.26 ± 0.04	
$p\text{-CH}_3$	$CHCl_3$		3.20 ± 0.16
	60% TCE 40% $CHCl_3$		3.59 ± 0.02
	60% CH_3OH 40% $CHCl_3$		3.98 ± 0.12

[a] Normalized to the given value in pure chloroform.

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(6) R. P. Cross and P. Fugassi, THIS JOURNAL, **71**, 223 (1949).

(7) For σ values, as constants representative of the extent of possible electron supply for these groups, see L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.

(8) T. A. Geissman and S. L. Friess, THIS JOURNAL, **72**, 3893 (1950).

(9) T. Tasaki, *Acta Phytochim.*, **3**, 259 (1927).

(10) H. Fernholz, *Ber.*, **84**, 110 (1951).

form, 60% *sym*-tetrachloroethane (TCE); and (3) 40% chloroform, 60% methanol. The results of these runs are shown in Table IV.

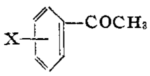
It is seen from Table IV that an increase in polarity of the solvent, whether caused by addition to chloroform of either methanol or TCE brings about an intrinsic increase in rate, with the effect being more pronounced for ketones characterized by first order kinetics. Tentatively, these solvent effects would seem to favor a polar slow step (or steps) for the reaction involving the disappearance of peracid.

Energies, Enthalpies and Entropies of Activation.—For a series of six of the substituted acetophenones, rate runs in pure chloroform were made at three temperatures, to obtain the thermodynamic quantities of activation. From the rate data, Arrhenius energies of activation were first obtained graphically, in the usual manner. From these data and the normalized rate constants at 31.00 ± 0.01°, the quantities $\Delta H^{\pm}$, $\Delta S^{\pm}$ and $\Delta F^{\pm}$ for this temperature were calculated. The results are shown in Table V.

TABLE V

ENERGIES, ENTHALPIES AND ENTROPIES OF ACTIVATION

Temperatures employed: 25.01 ± 0.03°, 31.00 ± 0.01°, 35.79 ± 0.01°

Ketone 	$E^{\text{Arr.}}$, (kcal./mole)	$\Delta H^{\pm}$, (kcal./mole)	$\Delta F^{\pm}$,[a] (kcal./mole)	$\Delta S^{\pm}$[a] (*e.u.*)
p-OCH_3	11.4 ± 0.3	10.8 ± 0.3	23.7	−42
p-CH_3	11.4 ± .3	10.8 ± .3	24.2	−44
m-OCH_3	14.9 ± .5	14.3 ± .5	24.3	−33
p-Cl	15.0 ± .3	14.4 ± .3	25.6	−37
p-OAc	14.0 ± 1.4	13.4 ± 1.4	25.5	−40
m-Br	13.9 ± 1.4	13.3 ± 1.4	25.6	−40

[a] Evaluated at 31.00 ± 0.01°.

From the data of Table V several interesting points are to be noted. First, regardless of reaction order or magnitude of rate constant, the entropy of activation[11] for each ketone reaction is negative and unusually large. Further, the $E^{\text{Arr.}}$ and $\Delta H^{\pm}$ values for those ketones whose *p*-substituents are strongly electron-donating in character are significantly lower than the remainder of the series.

The large negative values observed for $\Delta S^{\pm}$ would seem to demand a precise orientation of atoms and a fairly high degree of rigidity in the transition state, as compared to the reactants in the rate-determining process. This situation might perhaps be expected for a step involving addition to the carbonyl group, as outlined below.

Mechanism of Reaction.—In an attempt to correlate the previously noted facts regarding (1) the variation in order of reaction with changing nuclear substitution, (2) the acceleration of reaction rates by increased polarity of the medium, and (3) the catalysis by weak acids, the following general scheme is advanced as an over-all reaction mechanism.

$$\text{Peracid} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \begin{array}{c} C_6H_5COO^- + OH^+ \\ \text{or } C_6CH_5OOH + \underset{\cdot\cdot}{\ddot{O}}: \end{array} \qquad (1)$$

$$\text{Ketone} + OH^+ \text{ (or } \underset{\cdot\cdot}{\ddot{O}}:) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{complex A} \qquad (2)$$

$$\text{Ketone} + \text{peracid} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{complex B} \qquad (3)$$

$$\text{Complex A} \xrightarrow{k_4} \text{product} + H^+ \qquad (4)$$

$$\text{Complex B} \xrightarrow{k_5} \text{product} + C_6H_5COOH \qquad (5)$$

It is considered that either the peracid itself in step (3), or some entity derived from it such as $\underset{\cdot\cdot}{\ddot{O}}:$ or $\underset{\cdot\cdot}{\ddot{O}}:H^+$ in step (2), can react with ketone to ultimately furnish ester product, and that the sequence of reactions in the above set, employed by any given ketone, determines its over-all order of reaction.

In these reactions, it is to be expected that step (3) would be catalyzed by acid if it corresponds to a normal carbonyl addition reaction, and the occurrence of first order, acid-catalyzed reactions would seem to demand that step (1) also be an acid-catalyzed step.

In the above general mechanism, if complex A, complex B and OH^+ or $\underset{\cdot\cdot}{\ddot{O}}:$ are considered as unstable intermediates, then the general rate equation can be developed using the customary steady-state assumptions.

First, from the above set of equations

$$-\frac{d(\text{peracid})}{dt} = k_1(\text{peracid}) + k_3\,(\text{peracid})(\text{ketone}) - k_{-3}(\text{complex B}) - k_{-1}(C_6H_5COO^-)(OH^+) \qquad (6)$$

Also, for steady-state concentrations

$$(\text{complex A}) = \frac{k_2(\text{ketone})(OH^+)}{k_{-2} + k_4} \qquad (7)$$

$$(\text{complex B}) = \frac{k_3(\text{ketone})(\text{peracid})}{k_{-3} + k_5} \qquad (8)$$

$$(OH^+) = \frac{k_1(\text{peracid})}{k_{-1}(C_6H_5COO^-) + k_2(\text{ketone}) - \left(\frac{k_{-2}k_2\,(\text{ketone})}{(k_{-2} + k_4)}\right)} \qquad (9)$$

Substitution of (7), (8) and (9) into (6) lead to

$$-\frac{d(\text{peracid})}{dt} = k_1(\text{peracid}) \times \left[\frac{k_2(\text{ketone}) - \left(\frac{k_{-2}k_2\,(\text{ketone})}{k_{-2} + k_4}\right)}{k_{-1}(C_6H_5COO^-) + k_2(\text{ketone}) - \left(\frac{k_{-2}k_2\,(\text{ketone})}{k_2 + k_4}\right)}\right] + k_3(\text{ketone})(\text{peracid}) \left(\frac{k_5}{k_{-3} + k_5)}\right) \qquad (10)$$

If in chloroform solution the reasonable assumption is made that $k_1(C_6H_5COO^-) << k_2$ (ketone), then (10) reduces to

$$-\frac{d(\text{peracid})}{dt} = k_1\,(\text{peracid}) + k_3(\text{ketone})(\text{peracid}) \left(\frac{k_5}{k_{-3} + k_5}\right) \qquad (11)$$

In equation (11), if k_1 is quite large compared to k_3, or alternatively if k_{-3} is quite large compared to k_5, then (11) reduces to the first order kinetic behavior observed for *p*-chloroacetophenone, etc. On the other hand, if $k_1 << k_3$ and k_{-3} is small, then

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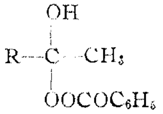
[11] For a discussion of this quantity see S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 22.

second order kinetics result from (11), as for example with *p*-methoxyacetophenone. Finally, where neither of these extremes hold, as is the case with unsubstituted acetophenone, the mixed mechanism predicted by (11) is actually observed.

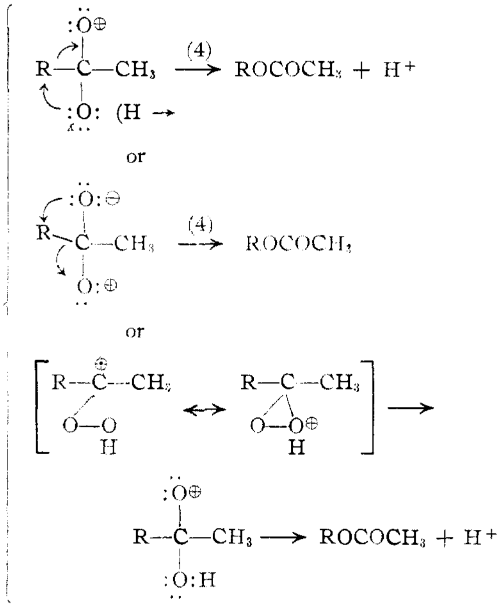
With respect to the nature of complexes A and B, it has previously been noted[5] that B could reasonably be the carbonyl addition product



$R-C(OH)(OOCOC_6H_5)-CH_3$

Several possibilities for complex A can be written, as intermediates which undergo the rearrangement step (4) to give ester product. These possibilities include[1,4]

complex A



Experimental

Preparative Scale Runs.—The ketones required for this study were prepared by standard methods and purified before use by distillation or recrystallization.

In a typical run of the series given in Table I, a weighed amount of ketone was dissolved in a volume of standardized ice-cold chloroform solution of perbenzoic acid containing that excess of peracid which results in the initial concentration ratio indicated. The reaction mixture was swirled at intervals and set aside in the dark. After consumption of one molar equivalent of peracid, as indicated by iodimetric titration of a one-ml. aliquot, the benzoic and residual perbenzoic acids were removed by extraction with 1 *M* sodium bicarbonate solution, followed by a water wash. The chloroform solution was then dried over anhydrous sodium sulfate, and the solvent distilled. The substituted acetate was either fractionally distilled or recrystallized from a suitable solvent. Mixed melting points of the solid esters with authentic samples gave no observed depressions of melting point, furnishing evidence of product purity. Each liquid product was saponified, and solid derivatives of the phenolic fractions prepared, for further characterization of these esters and independent checks on yields.

Rate Runs.—In a representative rate run, a weighed amount of the ketone concerned was placed in a 50-ml. glass-stoppered volumetric flask used for the reaction. To this was added an aliquot of a standardized perbenzoic acid solution[12] in dry chloroform, and the mixture made to volume with pure dry chloroform. The flask and contents were immersed in a constant temperature bath held to ±0.10° in most cases,[13] and after attainment of the bath temperature zero time was recorded and the first two-ml. aliquot taken for iodimetric analysis for residual perbenzoic acid content.[5] The reactions were studied to approximately the 20% completion point, and the detailed kinetic analysis of the data for first and second order conformity made graphically in the standard way, employing runs at varying initial concentrations of reactants.

In runs designed to investigate any given factor, identical aliquots of the same peracid solution were used, to keep the amount of acid catalyst at a constant level.

The effect of acid catalysis was noted by the rates of runs to which either benzoic or acetic acid in weighed amounts had been added before the peracid aliquot was pipetted in to start the reaction.

In runs in which methanol or *sym*-tetrachloroethane (TCE) was employed as part of a mixed solvent, the ketone was first dissolved in somewhat less than the required amount of this solvent, an aliquot of peracid in chloroform added, the mixture made to volume with the first solvent, and then finally thermostated. This procedure was adopted to lead to the minimum contact time of peracid with methanol, and hence to a minimum loss of peracid activity by esterification.

Acknowledgment.—The authors wish to express their appreciation to Beaunit Mills for the fellowship grant which supported a portion of this work.

Bethesda 14, Md. Received February 19, 1951

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[12] G. Braun, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 434.

[13] In the runs used to ascertain $\Delta S^{\ddagger}$ etc., the baths were controlled to at least ±0.03°.