ml. of water. This aqueous mixture was extracted five times with 50-ml. portions of methylene chloride to yield 5.0 g. (0.032 mole) of recovered *p*-chloroacetophenone. The aqueous solution was acidified with 15 ml. of concentrated hydrochloric acid and extracted overnight with ether in a continuous extraction apparatus. The ether extract was dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was diluted to 100 ml. with glacial acetic acid and analyzed as described below. The analysis showed that 2.08 × 10^{-2} mole of *p*-chlorophenylacetate and 5.9 × 10^{-4} mole of methyl *p*-chlorobenzoate were produced in the reaction.

Analytical Procedure for the Determination of *p*-Nitrobenzoic Acid and *p*-Nitrophenol.—Solutions of *p*-nitrophenol and of *p*-nitrobenzoic acid (1 × 10^{-4} *M*) were prepared in glacial acetic acid solvent and the ultraviolet absorption spectra of these solutions were determined with a Beckman model DK-1 spectrophotometer using 1-cm. silica cells. *p*-Nitrophenol was found to have an extinction coefficient of 1.08 × 10^4 at λ_{max} 308 mμ while *p*-nitrobenzoic acid absorbed most strongly at 259 mμ with an extinction coefficient of 1.28 × 10^4. Since the absorption of *p*-nitrobenzoic acid was negligible at 308 mμ, mixtures of the two compounds could be analyzed directly for *p*-nitrophenol by determining the absorbence of the unknown solution at 308 mμ. *p*-Nitrobenzoic acid was determined by subtracting 17% of the absorbence of the unknown solution at 308 mμ from its absorbence at 259 mμ. Several known mixtures were analyzed in this manner with great accuracy (±2% error).

Analytical Procedure for the Determination of *p*-Chlorophenol and *p*-Chlorobenzoic Acid.—The spectra of both pure materials were determined as for *p*-nitrophenol and *p*-nitrobenzoic acid. *p*-Chlorophenol had λ_{max} 281 mμ and an extinction coefficient of 1.70 × 10^3 while *p*-chlorobenzoic acid had λ_{max} 248 mμ and an extinction coefficient of 1.27 × 10^4. The *p*-chlorobenzoic acid did not interfere with the *p*-chlorophenol absorbence at 281 mμ. Therefore, the concentration of *p*-chlorophenol was determined directly from the absorbance of the unknown solution at 281 mμ. The absorbance of *p*-chlorobenzoic acid was determined by subtracting 6% of the absorbance of the solution at 281 mμ from the absorbance at 248 mμ. The precision of the method was shown to be excellent since known mixtures could be analyzed to within ±2%.

HUNTSVILLE, ALA.

[CONTRIBUTION FROM THE ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

A Re-examination of the Peroxyacid Cleavage of Ketones. II. Kinetics of the Baeyer–Villiger Reaction

BY M. FREDERICK HAWTHORNE[1] AND WILLIAM D. EMMONS

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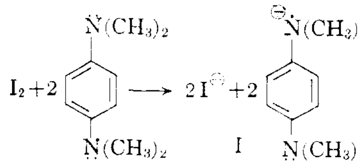
The kinetics of the reaction of a series of ketones with trifluoroperoxyacetic acid has been determined in ethylene chloride and 10:1 acetonitrile–ethylene chloride solvents. The results lead to the conclusion that the rate-determining step of the Baeyer–Villiger reaction is the acid-catalyzed decomposition of the peroxyacid–ketone adduct.

The quantitative reaction of trifluoroperoxyacetic acid with ketones[2] allowed a study of the kinetics of this reaction to be made and the results of this investigation are reported here. Our prime objective in this study was identification of the rate-controlling step and this problem was attacked in several ways. Among the experimental approaches were: (1) an examination of acid catalysis, (2) an attempted correlation of reaction rates with migratory abilities of the aryl or alkyl groups attached to the ketonic carbonyl group, (3) an attempted correlation of carbonyl group reactivity in other reactions with rates of Baeyer–Villiger reactions, (4) the effect of solvent type on ketone reactivity and (5) a study of rate as a function of peroxyacid structure.

Results

Kinetic Methods.—Phenyl alkyl ketones and substituted acetophenones, with which product distributions had been previously determined, were examined kinetically as were the simple cycloalkanones with from five to seven ring members and a series of methyl alkyl ketones. Two reaction solvents of greatly different character were employed: ethylene chloride and 10:1 (volume) acetonitrile–ethylene chloride. In every case the reaction temperature was 29.8°, a temperature which allowed rate measurements to be made throughout the wide spectrum of ketone reactivities encountered. The change in concentration of trifluoroperoxyacetic acid was followed as a measure of the extent of reaction. The analytical method employed was an adaptation of a previously described method[3] which involved the following reactions and the spectrophotometric determination of I.

$$CF_3CO_3H + H^{\oplus} + 2I^{\ominus} \longrightarrow CF_3CO_2^{\ominus} + I_2 + H_2O \qquad (I)$$



(II)

Kinetics Measurements in Acetonitrile–Ethylene Chloride Solution.—Owing to the fact that trifluoroperoxyacetic acid was stable in acetonitrile solution it was possible to carry out rate measurements in this highly polar and nucleophilic solvent. Rate measurements were carried out under pseudo first-order conditions using a large excess of ketone and varied amounts of trifluoroacetic acid catalyst. The observed rates were found to fit the rate expression (1).

$$-d[CF_3CO_3H]/dt = k_3[CF_3CO_2H][R_2CO][CF_3CO_3H] \qquad (1)$$

Since trifluoroacetic acid is a product of the reaction, it was not surprising to find that after approximately 25% reaction the pseudo first-order plots of log [CF_3CO_3H] *vs.* time developed curvature as would be required of an autocatalytic reaction.

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[1] Presented at the Sixth Reaction Mechanisms Conference, Swarthmore, Pa., September, 1956.

[2] M. F. Hawthorne, W. D. Emmons and Keith S. McCallum, THIS JOURNAL, **80**, 6393 (1958).

[3] M. F. Hawthorne, *ibid.*, **79**, 2510 (1957).

The rate constants were therefore evaluated from the linear, initial portions of such plots. This procedure was used since experimental uncertainties in the initial reactant concentrations and the measurement of instantaneous peroxyacid concentrations would not justify a more sophisticated treatment. The rate constants were reproducible to within ±10% over a fourfold range of initial ketone and acid catalyst concentrations. Table I illustrates the dependence of rate upon initial ketone and trifluoroacetic acid concentrations for three ketones which are representative of all the types studied. Table II presents the values of the third-order rate constants obtained in the same manner for all ketones studied in acetonitrile–ethylene chloride.

TABLE I

DEPENDENCE OF BAEYER–VILLIGER RATE UPON TRIFLUOROPEROXYACETIC ACID, TRIFLUOROACETIC ACID AND KETONE CONCENTRATIONS IN ACETONITRILE–ETHYLENE CHLORIDE AT 29.8°

Ketone	Initial concentrations, mole l.$^{-1}$ Ketone	Peroxy-acid	Trifluoro-acetic acid	k_3, l.^{2} mole^{-2} sec.$^{-1a}$
Acetophenone	0.198	0.077	0.117	1.58×10^{-3}
	.386	.076	.114	1.82
	.755	.084	.230	1.74
Acetone	1.580	.078	.117	7.35×10^{-4}
	1.580	.089	.240	7.65
	0.790	.078	.114	7.60
Cyclopentanone	1.09	.080	.122	2.72×10^{-3}
	0.52	.078	.361	2.58

[a] Initial values from first 30% of reaction.

TABLE II

COLLECTED RATE DATA FOR METHYL ALKYL KETONES, PHENYL ALKYL KETONES, CYCLOALKANONES AND SUBSTITUTED ACETOPHENONES IN ACETONITRILE–ETHYLENE CHLORIDE (10:1 VOLUME) AT 29.8°

Ketone series	R	k_3, l.^{2} mole^{-2} sec.$^{-1a}$
CH_3COR	Methyl	7.5×10^{-4}
	Ethyl	7.6×10^{-3}
	Isopropyl	5.7×10^{-3}
	t-Butyl	1.6×10^{-3}
	Cyclopropyl	1.3×10^{-3}
C_6H_5COR	Methyl	1.7×10^{-3}
	Ethyl	8.6×10^{-4}
	Isopropyl	9.1×10^{-4}
	t-Butyl	1.5×10^{-4}
	Neopentyl	5.2×10^{-4}
	Cyclohexyl	2.5×10^{-4}
	Cyclopentyl	4.1×10^{-4}
$\overline{(CH_2)_R\ C}{=}O$	4	2.7×10^{-3}
	5	6.1×10^{-2}
	6	1.3×10^{-2}
$CH_3COC_6H_5—R$	*p*-Methyl	2.9×10^{-3}
	Hydrogen	1.7×10^{-3}
	p-Chloro	5.3×10^{-4}
	p-Bromo	7.7×10^{-4}
	m-Nitro	1.7×10^{-4}
	p-Nitro	1.1×10^{-4}

[a] Reproducible to ±10%.

Kinetic Measurements in Pure Ethylene Chloride.—The kinetics of the reaction in ethylene chloride solvent were of a different character from those obtained in the presence of acetonitrile. Again the reactions were carried out under pseudo first-order conditions with a large excess of ketone and in the presence of varied concentrations of trifluoroacetic acid catalyst. Reactions were followed to 50–60% completion. It was observed that the pseudo first-order constants obtained *under these conditions* were independent of the initial concentration of ketone but gave first-order dependence on initial trifluoroacetic acid concentration. No evidence for autocatalysis by trifluoroacetic acid was obtained. The pseudo first-order rate constant was dependent upon the *identity* of the ketone and the rate-determining step must therefore involve this reactant. These results are explicable in terms of a transition state containing peroxyacid, ketone and acid catalyst if the ketone is essentially completely complexed by one of the other reactants. Under these conditions either (2) or (3) could represent the "true" rate law.

$$-d[CF_3CO_3H]/dt = k_2[CF_3CO_3H\text{-}R_2CO][CF_3CO_2H] \quad (2)$$

$$-d[CF_3CO_3H]/dt = k_2[CF_3CO_3H][CF_3CO_2H\text{-}R_2CO] \quad (3)$$

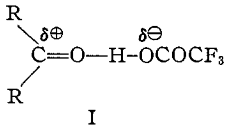
This problem was resolved by the detection of complexes of trifluoroacetic acid with the ketones. A considerable amount of heat was produced when solutions of the acid and ketone were mixed and the mixed solutions had ultraviolet spectra different from those of the constituents. Table III presents this spectroscopic evidence as obtained from the examination of six representative ketones in the presence and absence of trifluoroacetic acid in ethylene chloride solvent.

TABLE III

TRIFLUOROACETIC ACID–KETONE COMPLEXATION IN ETHYLENE CHLORIDE, N → π-TRANSITIONS IN PURE ETHYLENE CHLORIDE AND 0.1 *M* TRIFLUOROACETIC ACID IN ETHYLENE CHLORIDE

	Ethylene chloride		0.1 *M* CF_3CO_2H in ethylene chloride	
Ketone	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}
Cyclopentanone	295	19	280	24
Methyl ethyl ketone	278	18	268	21
Methyl cyclopropyl ketone	275	22	260	34
Cyclohexanone	288	18	275	24
Methyl isopropyl ketone	285	22	272	30
Acetophenone[a]	275	1000	290	1500

[a] Red shift attributed to π → π-transition.



I

That complexes such as I are formed is further indicated by the fact that *m*- and *p*-nitroacetophenone give approximately third-order Baeyer–Villiger kinetics in ethylene chloride. The carbonyl oxygen atoms of the ketones are too weakly basic for the extensive formation of the hydrogen bonded complex.

Nagakura, Minegishi and Stanfield have recently reported[4] a study of the N → π-transition of acetone in sulfuric acid of varying concentrations and reach similar conclusions as to the formation of complexes such as I. The red shift observed with acetophenone in trifluoroacetic acid corresponds to the red shift observed by these authors for mesityl oxide in sulfuric acid and is probably due to a π → π-type transition.

The absence of detectable autocatalysis up to 50–60% reaction was shown in part to be due to the fact that trifluoroacetic acid is consumed by transesterification with the ester produced in the reaction. Reaction 4 was shown to be rapid at room temperature.

$$RCOOR' + CF_3CO_2H \overset{K}{\rightleftarrows} RCOOH + CF_3COOR' \quad (4)$$

Mixing of dilute solutions of ethyl acetate and trifluoroacetic acid in ethylene chloride followed by immediate infrared analysis of the mixture (about 2 minutes reaction time) showed that the system given in (4) had reached equilibrium and that K was equal to 0.57 for this reaction. It therefore appears as though interaction of the reaction products effectively removes a large portion of the strongly acidic by-product, thereby suppressing the autocatalytic effect. No evidence for complexes containing ester and trifluoroacetic acid was sought or found. However, such complexes might well exist.

Table IV presents data for four representative ketones which illustrate the dependence of the rate of consumption of trifluoroperoxyacetic acid upon the initial concentration of ketone–trifluoroacetic acid complex when the ketones were in large excess. Table V presents the collected rate data for all ketones studied in ethylene chloride.

TABLE IV

DEPENDENCE OF BAEYER–VILLIGER RATE UPON INITIAL KETONE–TRIFLUOROACETIC ACID COMPLEX CONCENTRATIONS IN ETHYLENE CHLORIDE AT 29.8°

Ketone	Initial concentrations, mole l.$^{-1}$ Ketone	Trifluoroacetic acid	Peroxyacid	k_2, l. mole^{-1} sec.$^{-1a}$
Acetophenone	0.775	0.198	0.084	2.64×10^{-2}
	.193	.117	.077	2.82×10^{-2}
	.386	.114	.076	3.15×10^{-2}
Acetone	1.600	.128	.085	1.74×10^{-3}
	1.600	.259	.079	2.03×10^{-3}
	0.800	.128	.085	1.86×10^{-3}
Methyl isopropyl ketone	1.05	.118	.078	3.34×10^{-2}
	1.05	.259	.078	3.32×10^{-2}
	0.500	.118	.078	3.71×10^{-2}
Cyclopentanone	1.09	.119	.078	1.55×10^{-2}
	1.08	.122	.081	1.86×10^{-2}
	0.54	.238	.078	1.78×10^{-2}

[a] From initial 50–60% reaction.

Reaction Rates with Peroxyacetic Acid.—Since the Baeyer–Villiger reaction is acid catalyzed,[5] comparison of the reactivity of different peroxyacids must be carried out under conditions of comparable acidity. In order to accomplish this end we measured the rate of reaction of cyclohexanone with peroxyacetic acid in ethylene chloride in the presence of trifluoroacetic acid. These reactants were chosen for the following reasons: peroxyacetic acid is prepared easily in anhydrous solution and it is well known that this acid is much less reactive in other oxidation reactions than is trifluoroperoxyacetic acid. Cyclohexanone was employed since this ketone is the most reactive of those studied thus lending more convenience to the measurements. Ethylene chloride was employed due to the fact that the reaction is faster in this solvent and the role of strong acid catalyst (trifluoroacetic acid) could be observed through its complex with cyclohexanone. Results reported in the previous paper indicated that trifluoroacetic acid did not exchange active oxygen with peroxyacetic acid under the conditions of these rate experiments. The kinetic results obtained in this system are given in Table VI.

TABLE V

COLLECTED RATE DATA FOR METHYL ALKYL KETONES, PHENYL ALKYL KETONES, CYCLOALKANONES AND SUBSTITUTED ACETOPHENONES IN ETHYLENE CHLORIDE AT 29.8°

Ketone series	R	k_2, l. mole^{-1} sec.$^{-1a}$
CH_3COR^b	Methyl	1.8×10^{-3}
	Ethyl	4.4×10^{-2}
	Isopropyl	3.4×10^{-2}
	t-Butyl	1.4×10^{-2}
	Cyclopropyl	2.8×10^{-3}
C_6H_5COR	Methyl	2.7×10^{-2}
	Ethyl	2.3×10^{-2}
	Isopropyl	2.0×10^{-2}
	n-Propyl	2.1×10^{-2}
	t-Butyl	7.7×10^{-3}
	Neopentyl	1.3×10^{-2}
	Cyclohexyl	5.5×10^{-3}
	Cyclopentyl	8.5×10^{-3}
$\overline{(CH_2)_R\ \ C}{=}O$	4	1.7×10^{-2}
	5	3.2×10^{-1}
	6	5.8×10^{-2}
$CH_3COC_6H_5R$	*p*-Methyl	4.6×10^{-2}
	Hydrogen	2.9×10^{-2}
	p-Chloro	1.7×10^{-2}
	p-Bromo	1.8×10^{-2}
	m-Nitro	[c]
	p-Nitro	[c]

[a] Reproducible to ±10%. [b] Diethyl ketone, $k_2 = 3.16 \times 10^{-2}$. [c] Kinetics show ketone concentration dependences are not clearly second or third order over-all.

It is apparent that within experimental error these results best fit rate expression 5. Acetic acid appears to be ineffective as a catalyst under these conditions. These results clearly show that trifluoroperoxyacetic acid is about two hundred times as reactive as peroxyacetic acid with cyclohexanone under the same conditions of acid catalysis.

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(4) S. Nagakura, A. Minegishi and K. Stanfield, THIS JOURNAL, **79**, 1033 (1957).

(5) In addition to the presently described work, acid catalysis has been observed previously by the following workers: (a) S. L. Friess, *ibid.*, **71**, 2591 (1949); (b) S. L. Friess and A. H. Soloway, *ibid.*, **73**, 3970 (1951); (c) S. L. Friess and R. Pinson, *ibid.*, **74**, 1302 (1952); (d) Y. Yukawa and T. Yokoyama, *Mem. Inst. Sci. Ind. Research Osaka Univ.*, **9**, 180 (1952); (e) *J. Chem. Soc. Japan*, **73**, 371 (1952).

TABLE VI

KINETICS OF THE TRIFLUOROACETIC ACID-CATALYZED REACTION OF PEROXYACETIC ACID WITH CYCLOHEXANONE IN ETHYLENE CHLORIDE AT 29.8°

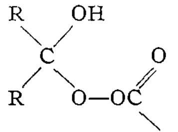
Initial concentrations, mole l.$^{-1}$				
Cyclohexanone	Trifluoroacetic acid	Acetic acid	Peroxyacetic acid[a]	k_2, l. mole^{-1} sec.$^{-1}$
0.945	0.114	0.143	0.095	1.63×10^{-3}
.477	.114	.143	.095	1.49×10^{-3}
.945	.228	.143	.095	1.40×10^{-3}

[a] No hydrogen peroxide or trifluoroperoxyacetic acid could be detected by ceric sulfate titration.

$$-d[CH_3CO_3H]/dt = k_2[R_2CO\text{-}HOCOCF_3][CH_3CO_3H] \quad (5)$$

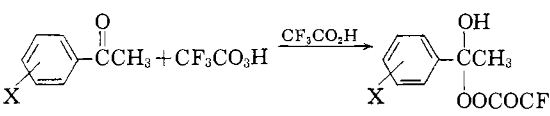
Discussion

The experimental results presented above and in previous work[5] prove that the Baeyer–Villiger reaction is acid catalyzed in every investigated instance. The rate-determining transition state must therefore be composed of ketone, peroxyacid and acid catalyst although this fact does not specify whether the rate-determining step is the bond making addition of peroxyacid to a protonated carbonyl group or the bond breaking, acid-catalyzed, heterolysis of the Criegee intermediate A. The following discussion will attempt to resolve this problem.

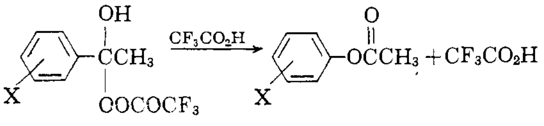


A

Hammett Treatment of Substituted Acetophenones.—Hammett plots[6] of the rate data for the substituted acetophenones are shown in Figs. 1 and 2. It is seen that these data produce reasonably well defined lines, although the spread of σ-values covered in each is not extremely large. However, the ρ-values obtained in these two plots are both negative and similar in magnitude. Since it was shown in the preceding paper that the poorest migrating group of this series, namely, p-nitrophenyl, migrated to such an extent as to produce 87% p-nitrophenyl acetate in ethylene chloride solution, it may be assumed that for all practical purposes the rate measurements were made on the processes represented by either 6a or 6a plus 6b.



(6a)



(6b)

Acid-catalyzed carbonyl addition reactions such as 6a normally give moderate and positive ρ-values[7] while a moderately large and negative value is observed in the present instance. The result implies that in this series of reactions the free energy of activation of process 6b makes a significant contribution to the over-all free energy of the

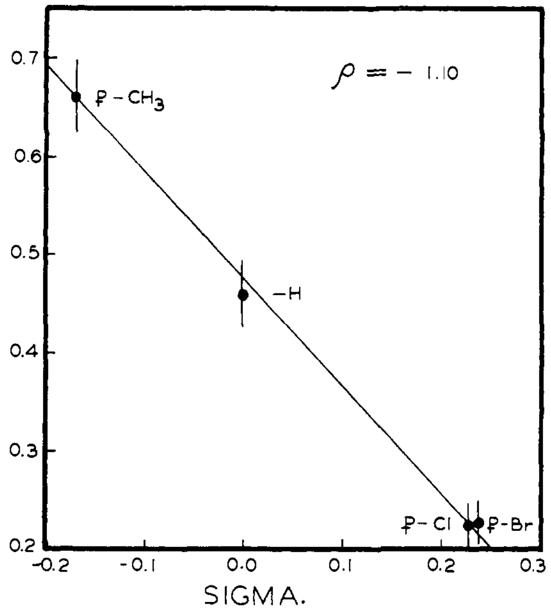


Fig. 1.—Hammett plot of p-substituted acetophenone rates in ethylene chloride at 29.8°.

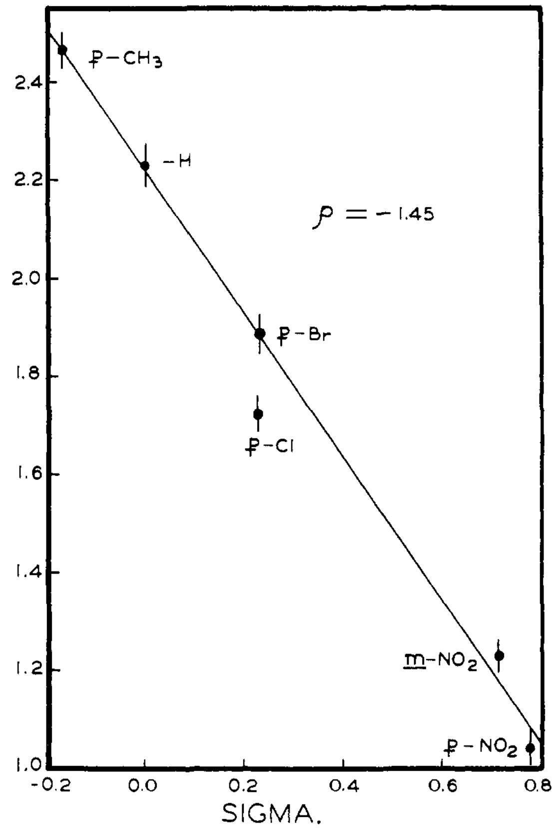


Fig. 2.—Hammett plot of substituted acetophenone rates in acetonitrile at 29.8°.

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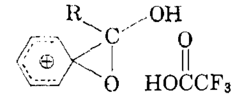
(6) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.

(7) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953), lists ρ-values for acid-catalyzed hydrolysis of ethyl benzoates in 60% ethanol, 0.144; for semicarbazone formation with acetophenones, 0.91; for addition of N,N-dimethylaniline to the carbonyl group of acetophenones, 0.83.

reaction and that process 6b is the rate-controlling step of the reaction and proceeds through a transition state such as I.



I

Correlation of Baeyer–Villiger Reaction Rates with Carbonyl Group Reactivity and Migratory Aptitudes.—As recently shown by Fitzpatrick and Gettler,[8] the rates of simple carbonyl addition reactions such as semicarbazone formation and oximation may be correlated by a simple linear free energy relationship. In the cited instance the rates of these two reactions were successfully related for all compounds for which data was available, *i.e.*, cyclohexanone, acetone, cyclopentanone, diethyl ketone, pinacolone and acetophenone. If the rate-determining step of the Baeyer–Villiger reactions were the slow addition of peroxyacid to the protonated carbonyl group of a ketone, then one might reasonably expect a linear relationship to exist between the free energies of activation for the Baeyer–Villiger reaction and the free energy of activation for oximation of the same ketones. Figure 3 clearly shows that such a relationship does not exist: cyclopentanone, methyl ethyl ketone and cyclohexanone appear to form a rough linear relationship; acetophenone, pinacolone, methyl isopropyl ketone and acetone deviate.[9] These deviations may be rationalized on the basis of fast and reversible formation of the Criegee intermediate A with a free energy of formation ΔF_A, followed by a rate-determining decomposition of A with a free energy of activation of $\Delta F_M^{\ddagger}$. The observed Baeyer–Villiger rate constants, *k*, are thus defined as in (7).

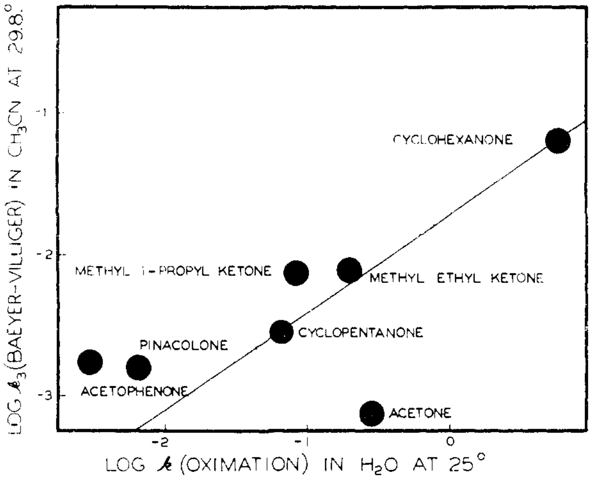


Fig. 3.—Attempted correlation of Baeyer–Villiger rates with corresponding oximation rates.

$$-RT \ln k = \Delta F_A + \Delta F_M^{\ddagger} = \Delta F^{\ddagger} \qquad (7)$$

If the Criegee intermediate A is a species of high energy content, the transition state for its destruction will resemble A itself. Therefore, $\Delta F_M^{\ddagger}$ will be small and $\Delta F^{\ddagger}$ will be *roughly* proportional[10] to ΔF_A. However, deviations will be expected, especially in cases in which the transition state for decomposition has made appreciable progress away from the intermediate. In the cases which apparently correlate with oximation rates, $\Delta F_M^{\ddagger}$ may vary very little since the reactions of these ketones involved alkyl groups which have similar migratory abilities relative to phenyl.[11] If this is the case, then (8) would express $\Delta F^{\ddagger}$ in relation to ΔF_A.

$$\Delta F^{\ddagger} = \Delta F_A + \text{constant} \qquad (8)$$

In the case of acetone methyl migrates and ΔF_M must be considerably larger than in the cases discussed above. The relationship 8 is no longer obeyed and acetone deviates from a correlation in the sense of showing extra sluggishness in the Baeyer–Villiger reaction.[9]

The reactions of acetophenone, pinacolone and methyl isopropyl ketone all involve the migration of groups which migrate more readily then the primary alkyl groups. It is not surprising then to find that these ketones react more rapidly in the Baeyer–Villiger reaction than would be predicted be comparison with their oximation rates. In these cases $\Delta F_M^{\ddagger}$ is probably smaller than $\Delta F_M^{\ddagger}$ for primary alkyl group migration.

Baeyer–Villiger Reaction Rates and Solvent Effects.—Figure 4 is a plot relating the free energies of activation of a series of Baeyer–Villiger reactions in the two solvents used in this investigation. One would expect an excellent correlation of the rates of a series of closely related reactions in two solvents if the mechanisms were rather rigidly fixed. The fact that there are significant deviations implies that the mechanism is fairly complicated. One way of accounting for the absence of a good, general correlation would be to assume that the rate-determining step is sometimes formation of the Criegee intermediate and sometimes decomposition of that species. However, such an assumption is probably not necessary. The mere fact that the over-all rate constant is most likely the product of the equilibrium constant for the formation of the Criegee intermediate and the rate constant for the decomposition of the intermediate ($K_A k_d$) is probably sufficient to account for the result. On the whole, points for those ketones which would be expected to have large values of K_A fall below the best line in Fig. 4 and those which should have smaller equilibrium constants fall above the line. Since the ketones are complexed by trifluoroacetic acid

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(8) W. Fitzpatrick and J. D. Gettler, THIS JOURNAL, **78**, 530 (1956).

(9) Y. Yukawa and T. Yokayama (refs. 5 d and e) have made similar comparisons of Baeyer–Villiger reaction rates using peroxyacetic acid and the corresponding oximation rates for a series of ketones. Their data show that those ketones which have high oximation rates have low rates in the Baeyer–Villiger reaction. This fact suggested to those authors that the rate-determining step of the Baeyer–Villiger reaction was not carbonyl addition of peroxyacid. They also observed that although cyclohexanone and acetone gave very similar rates of oximation, cyclohexanone was forty times faster in the Baeyer–Villiger reaction.

(10) These arguments are based on the Hammond postulate, THIS JOURNAL, **77**, 334 (1955), which qualitatively relates reaction rates with the corresponding equilibria.

(11) Compare the migratory abilities of ethyl and *n*-propyl *vs.* phenyl which are given in the preceding paper; M. F. Hawthorne, W. D. Emmons and K. S. McCallum, *ibid.*, **80**, 6393 (1958).

in ethylene chloride and are not highly associated in acetonitrile, prediction of the variations of K_A in the two media is not easy. If one assumes that $\Delta \log K_A$ is constant for the change in solvent a sort of rationalization can be had. The rate constant for decomposition of the intermediate should be less sensitive to ionizing power of the solvent when the migrating group is aryl and, accordingly, the rates of reaction of aryl ketones are decreased more than would be expected by a change to a better ionizing medium. Conversely, ketones, such as acetone and cyclopropyl methyl ketone, which contain only poor migrating groups, react relatively rapidly in the polar solvent which is better able to supply much needed solvation in the ionization process. On the whole we are best satisfied by a picture in which variations in K_A dominate the general trends in reactivity with the general trend being modified by smaller variations in k_d (since $\Delta F_M^{\ddagger}$ is rather small in all cases).

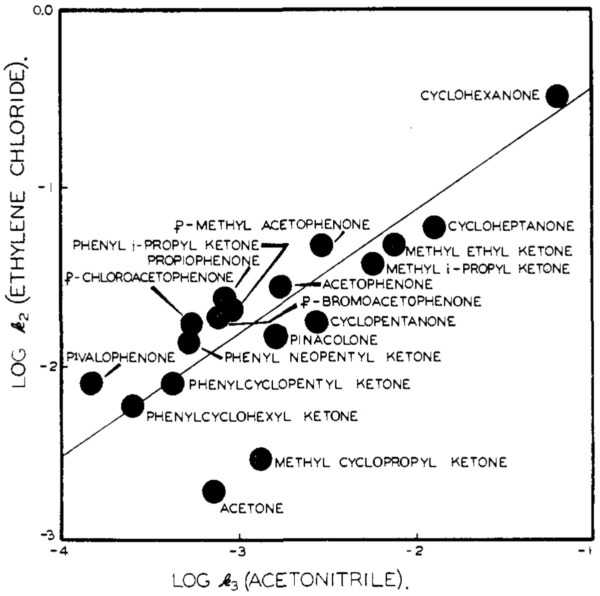

Fig. 4.—Correlation of Bayer–Villiger rates in acetonitrile with rates in ethylene chloride at 29.8°.

The Effect of Leaving Group on Reaction Rate.—The reaction of cyclohexanone with peroxyacetic acid in the presence of trifluoroacetic acid and in ethylene chloride solvent at 29.8° is slower by a factor of about 200 than the corresponding reaction using trifluoroperoxyacetic acid. Since the comparison was carried out *using the same acidic catalyst*, the difference in rate must be attributed to differences in the peroxyacid structures. Since we can conceive of no argument which would account for the weakly nucleophilic trifluoroperoxyacetic acid being more reactive than peroxyacetic acid in carbonyl addition, the observed difference in reactivity is the strongest argument in favor of acid-catalyzed decomposition of the Criegee intermediate. In the latter reaction the high reactivity of trifluoroacetic acid as a leaving group gives a clear explanation of the relatively great reactivity of trifluoroperoxyacetic acid.

Experimental

Materials.—Ethylene chloride was purified as described in the previous paper.[2] Acetonitrile was Eastman "spectrograde" which was distilled from phosphorus pentoxide before use. Trifluoroacetic acid and anhydride were obtained in a high degree of purity and used directly. Hydrogen peroxide ("90%") was standardized before use by titration with standard potassium permanganate solution. All ketones were obtained commercially or synthesized by standard methods which are in the literature. In every case the ketones were either recrystallized to constant melting point or distilled through a Heli-pak column of fifty plates efficiency. N,N,N′,N′-Tetramethyl-*p*-phenylenediamine dihydrochloride was Eastman Kodak Co. White label grade.

Kinetic Procedures.—Solutions of trifluoroperoxyacetic acid containing trifluoroacetic acid in ethylene chloride were prepared as follows: Approximately 0.8 g. of 88% hydrogen peroxide was weighed into a 25-ml. volumetric flask containing 15 ml. of dry ethylene chloride. For each gram of 88% hydrogen peroxide taken, 4.89 ml. of freshly distilled trifluoroacetic anhydride was added with shaking and cooling from a micro-buret protected from atmospheric moisture by a drying tube. Solutions were made up to 25.0 ml. at 29.8° by the addition of ethylene chloride. Active oxygen was titrated as hydrogen peroxide with standard potassium permanganate or ceric sulfate. Calculated titers normally agreed with the observed titers to within 3%. The concentrations of acid and peroxyacid present in these solutions were calculated by the equation

$$[CF_3CO_2H]_0/[CF_3CO_3H]_0 = 1.52$$

and $[CF_3CO_3H]_0 = 1.035$ *M* per gram of 88% hydrogen peroxide used in 25 ml. of solution. The calculation takes account of acid formed by reaction of anhydride with water present in the hydrogen peroxide. The active oxygen titers remained constant for at least 12 hours at 29.8°.

Peroxyacetic acid was prepared from weighed amounts of 88% hydrogen peroxide and acetic anhydride as described in the previous paper. Trifluoroacetic acid was added before the final dilution to 25 ml.

Kinetic runs in 10:1 (volume) acetonitrile–ethylene chloride and pure ethylene chloride were carried out in essentially the same manner. A 0.2 to 1.5 *M* solution of a ketone was prepared in 25 ml. of either acetonitrile or ethylene chloride at 29.8°. In the former case, 10 ml. of this solution was transferred to a 25-ml. volumetric flask and 1.00 ml. of the stock solution of trifluoroperoxyacetic acid was added to initiate the reaction at zero time. At intervals, 2.00-ml. aliquots of the reaction solution were withdrawn and added rapidly to 5.00 ml. of a 10% sodium iodide–acetonitrile solution contained in a 10-ml. volumetric flask. The flask was shaken and allowed to stand for two minutes. A 0.050-ml. aliquot of the iodine solution then was diluted to 10 ml. with 80% aqueous methanol and about 100 mg. of an equal weight mixture of sodium acetate and N,N,N′,N′-tetramethyl-*p*-phenylenediamine was added and the flask was shaken. The optical density of the resulting solution of Würster blue was determined immediately at a fixed wave length of 622 mμ with a Beckman model DK-1 recording spectrophotometer. The rate constant was evaluated from a plot of log optical density *vs.* time to about 25% reaction.

When pure ethylene chloride was used as solvent the procedure was identical except that 2.00-ml. aliquots of reactant ketone stock solutions in ethylene chloride were treated at zero time with 0.200 ml. of stock peroxyacid solution in 10-ml. volumetric flasks. At intervals 5 ml. of 10% sodium iodide in acetonitrile was added and the iodine solution was allowed to stand for two minutes. The resulting solution was then analyzed spectrophotometrically as described above and the rate constant was obtained in the same manner to 60% reaction. In runs which required an initial concentration of trifluoroacetic acid higher than that provided by the preparation of the peroxyacid, weighed amounts of the acid were added to the stock trifluoroperoxyacetic acid solution just prior to the final dilution to 25 ml. with ethylene chloride. The rate of the reaction of cyclohexanone with peroxyacetic acid in ethylene chloride was followed in the same way.

Ultraviolet Study of Ketone–Trifluoroacetic Acid Complexes.—Each of the ketones of Table III was examined using 1-cm. silica cells in a Beckman model DK-1 recording, double-beam spectrophotometer between 220 and 300 mμ in two solvents; pure ethylene chloride and ethylene chloride 0.1 *M* in trifluoroacetic acid. Ketone concentrations were approximately 5 × 10^{-2} *M* except in the case of acetophenone which was 9×10^{-4} *M*. The maxima are recorded in Table III.

Transesterification in Ethylene Chloride.—Approximately 0.20 *M* solutions of ethyl acetate and trifluoroacetic acid were prepared in pure dry ethylene chloride and their spectra were determined in an 0.05-mm. sodium chloride cell with a model 21 Perkin–Elmer infrared spectrophotometer. The ester absorbed at 5.76 μ and the acid at 5.56 μ. Equal volumes of the two solutions were mixed and the spectrum was recorded within two minutes. Carbonyl stretching bands characteristic of acetic acid monomer and dimer appeared near 5.9 μ. From the intensity of the ethyl acetate band before and after reaching equilibrium, and by comparison with known standards, the equilibrium constant $K = [CF_3CO_2Et][CH_3CO_2H]/[CH_3CO_2Et][CF_3CO_2H]$ was evaluated as 0.57. Similar experiments with acetonitrile solutions gave no evidence of transesterification after 12 hours under the same conditions.

Oxidation of Acetone with Trifluoroperoxyacetic Acid.—A solution of trifluoroperoxyacetic acid was prepared from 8.2 ml. (0.3 mole) of 90% hydrogen peroxide, 50.8 ml. (0.36 mole) of trifluoroacetic anhydride and 100 ml. of ethylene chloride. This solution was cooled in an ice-bath while 11.6 g. (0.2 mole) of acetone in 25 ml. of ethylene chloride was added dropwise. The resulting solution was kept at 5–10° for 20 hours and then was allowed to stand 2 hours at room temperature. The excess peracid was destroyed by addition of 30 g. of octene-1. The product, methyl trifluoroacetate, was obtained by careful fractionation of the reaction mixture using a center-rod column equipped with a capacitance controller for automatic take off; 17 g. (70%) of methyl trifluoroacetate, b.p. 42–43°, was obtained.

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Structural Effects on the Polymerization of Lactams

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The polymerizability of a number of lactams to polyamides was determined. When combined with literature data, these studies showed that: (1) Water and alkali metal catalysts were equally potent at temperatures above 200° (2) Rings with 8 or 9 members polymerized in all cases studied. About half of those with 7 atoms polymerized, while 6- or 5-membered rings failed to polymerize except in the case of pyrrolidone. (3) Alkyl or aryl substituents on the ring always decreased polymerizability. Hetero atoms in the ring either did likewise or had no effect. A mechanism was proposed for the alkali-catalyzed polymerization which has as its key step the attack of a lactam anion on an N-acyl-lactam chain end. It was suggested that the most important factor determining lactam polymerizability is the rate of cyclization of intermediates to reform the lactam. The intermediate may be aminoacid or acylaminoacid in the water-catalyzed polymerization, or an ω-aminoacyllactam in the alkali-catalyzed polymerization.

The polymerization of cyclic monomers[1] has received less attention than addition and condensation polymerizations. The available information on this subject was summarized by Small[2] and by Dainton and Ivin.[3] The polymerization of lactams, exemplified by the transformation of 6-caprolactam into poly-6-caproamide, forms the subject of this paper.

Two types of catalyst, namely, water and alkali metals or their hydrides, previously found to be effective[4] for the polymerization of lactams, were used in this study. A number of other potential catalysts, for example BF_3-etherate, litharge, etc., were tested but no catalytic activity was observed. However, effective cocatalysts for both the water- and alkali-catalyzed polymerizations were found (see below). In general, polymerization was carried out using molten monomers, since no useful solvents were discovered. The melting points of both lactam and resultant polyamide proved to be limiting factors for successful polymerization. If the melting points were excessively high, decomposition and inadequate contact of monomer and catalyst occurred.

The lactams studied are listed in Table I, the results of previous investigations being included in order to provide as complete a picture as possible of this field at the present time. Some generalizations can be made from the polymerization results summarized in Table I: (1) Water and sodium hydride were equally effective catalysts at temperatures above 200°. At room temperature water was ineffective but sodium hydride was still potent. (2) Ring-opening polymerization of lactams was a restricted technique, the majority of lactams failing to polymerize. (3) Of the five 8- and 9-membered ring compounds examined, all polymerized. Approximately one-half of the various 7-membered ring compounds which have been studied to date polymerized. Of the 6-membered rings, only 2,5-diketopiperazine is known to polymerize to any degree. 2-Pyrrolidinone was the only 5-membered lactam which polymerized. (4) Aryl or alkyl substituents on a ring decrease polymerizability, especially if they are on the nitrogen atom of the lactam. (5) Hetero atoms in a lactam ring either reduce polymerizability or have no effect. (6) Thiolactams (iminethiones) are markedly less prone to polymerize than the corresponding lactams. (7) Decomposition is particularly serious for lactams with hetero atoms β to the carbonyl group.

If a lactam fails to polymerize, the cause may be either an unfavorable equilibrium or a slow rate. We believe that water or alkali metals and their hydrides are sufficiently powerful to establish equilibrium between monomer and polymer, except where decomposition is extensive, at least above 200°. The following paragraphs attempt to show that the

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[1] The expression "ring-opening polymerization" applies to polymerization mechanisms in which a ring adds to a growing chain.

[2] P. A. Small, *Trans. Faraday Soc.*, **51**, 1717 (1955).

[3] F. S. Dainton and R. J. Ivin, *Quart. Revs.*, **12**, 82 (1958).

[4] W. E. Hanford and R. M. Joyce, *J. Polymer Sci.*, **3**, 167 (1948).