TABLE IV

QUANTITIES COMPUTED FROM INTEGRATED RATE EQUATION USING ASSUMED k-VALUES

Time	$A + B$	m	$A + B$ at 7 half-lives	Time	$A + B$	m	$A + B$ at 7 half-lives
First group: $k_2 = 0.2$, $k_3 = 0.2$				Third group: $k_2 = 0.5$, $k_3 = 0.167$			
0.0	0.1000		0.00781[a]	0.0	0.1000		0.0167[a]
.3	.0746	0.974	.00759	.2	.0826	0.957	.0161
.6	.0567	.946	.00734	.4	.0694	.914	.0155
.9	.0439	.915	.00706	.6	.0593	.870	.0148
Second group: $k_2 = 0.6$, $k_3 = 0.4$							
0.0	0.1000		0.00720[a]				
.3	.0753	0.946	.00644				
.6	.0585	.894	.00571				
.9	.0467	.845	.00504				

[a] Based on $m = 1$

fluoroacetic acid has been allowed to proceed for seven "half-lives" based on an early value of m. The first two groups of values in Table IV approximately correspond to the situation observed experimentally since values of $A + B$ at seven "half-lives" based on m when $t = 0.3$ are 7.59 and 6.44% of the initial alkene content, respectively. If other evidence leads us to use a k_3 value of 0.2 ($k_3/k_1 = 0.2$), the tables show that the k_2 value which fits the experiment is also approximately 0.2. The slope at $t = 0.3$ is 0.974. Multiplying the m-value by 1000/974 gives k_1. Accordingly, the experimentally determined slope is corrected by this amount. If we incorrectly assign $k_3 = 0.4$, the slope is 0.946 and a correction factor of 1000/946 would be applied to the experimentally determined slope. Accordingly, the tables lead us to the satisfying conclusion that the corrected slopes have values which are not far from k_1 even if the estimated k_3/k_1 ratios are grossly inaccurate.

The third group of values with $k_2 = 0.5$ and $k_3 = 0.167$ illustrates the behavior of m when approximately 16% of the initial alkene is present after seven half-lives and $k_3 = 0.167$. It may be seen that multiplying m by 1000/957 gives k_1 at $t = 0.2$ and that multiplying m by 1000/914 gives k_1 at $t = 0.4$. Since 16% was approximately the maximum amount of alkene found at seven half-lives, this portion of Table IV illustrates the maximum

corrections used in obtaining k_1 values. All of the substituted hexenes (Fig. 1) except the cyano- and methoxyhexenes showed approximately 16% double bond content after seven "half lives." In practice the tables for $k_1 = 1$ may be used for any rate determination since only the k_3/k_1 and k_2/k_1 ratios affect the rate plots for reactions followed for a specific portion of a half-life, as judged from the amount by which the alkene concentration $(A + B)$ decreases during the time the reaction is followed.

Isomerization Products from Reaction of 1-Hexene with Trifluoroacetic Acid.—1-Hexene was allowed to react with a pure sample of trifluoroacetic acid, obtained by hydrolysis of the anhydride, for exactly $1/6$ of a half-life at 35°. A sample of the reaction mixture was immediately analyzed by gas chromatography on a 20-ft. tricresyl phosphate column. The amounts of cis-2-hexene and trans-2-hexene were determined by comparison with the gas chromatogram of a 0.1 M solution in acetic acid of a standard mixture consisting of 97% 1-hexene and 3% of a mixture of cis-2-hexene and trans-2-hexene. Based on the amounts found and the amount of 1-hexene which can be calculated to have undergone addition after $1/6$ of a half-life, values of k_2/k_1 (ratio of rearrangement to addition) could be calculated. Two experiments gave $k_2/k_1 = 0.35$ and 0.47, respectively. The cis to trans ratios in the rearranged alkene were found to be 1.42 and 1.72, respectively. At the short reaction time employed, reaction of the 2-hexenes with trifluoroacetic acid is negligible within the accuracy of the analyses. A short fore-column of firebrick impregnated with potassium carbonate and then coated with Carbowax 20 M was used in the gas chromatographic analysis.

Isomerization of 2-Hexyl Trifluoroacetate.—A 0.1 M solution of 2-hexyl trifluoroacetate in trifluoroacetic acid 0.125 M in sodium trifluoroacetate was placed in a 60° bath. After 12 days, 21% isomerization to 3-hexyl trifluoroacetate had occurred as shown by analysis of the products (as the corresponding alcohols) on a tris-2-cyanoethoxypropane column. At equilibrium, approximately 37% of 3-hexyl trifluoroacetate is present. Detailed consideration of this experiment indicates that substituent isomerization was not important for the trifluoroacetates used in our study.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TEXAS TECHNOLOGICAL COLLEGE, LUBBOCK, TEXAS]

The Decomposition of Acetyl Peroxide in Solution. III. Kinetics and Use of Radical Traps[1]

BY H. J. SHINE, J. A. WATERS,[2] AND D. M. HOFFMAN

The rates of decomposition of acetyl peroxide in a number of olefins, benzene, carbon tetrachloride, and cumene at several temperatures were measured. The rate constants for the first-order process do not differ markedly from solvent to solvent. Energies of activation of decomposition in the olefins are similar to those in benzene, carbon tetrachloride, and toluene. In particular, the rate constants for decomposition in cyclopentene and cyclohexene are essentially the same as each other. The rate of formation of cyclopentyl acetate was found to be about twice as large as that of cyclohexyl acetate. The effect of iodine, water, and 9,10-dihydroanthracene on the rate of decomposition of acetyl peroxide has been studied. Iodine lowers the rate in carbon tetrachloride, water increases the rate, while the effect of 9,10-dihydroanthracene varies with the solvent. Some similar experiments with benzoyl peroxide were carried out. Acetyl peroxide is hydrolyzed when heated in wet carbon tetrachloride. A product of hydrolysis was titrated iodometrically and is assumed to be peracetic acid. The hydrolysis by water makes ambiguous the "trapping" experiments with iodine–water reported earlier. Hydrolysis of benzoyl peroxide is comparatively minor. The effect of diphenylpicrylhydrazyl and galvinoxyl on benzoyl and acetyl peroxides is to decrease the extent of carbon dioxide formation. At high concentrations (near 10^{-2} M) of peroxide and scavenger the effect of diphenylpicrylhydrazyl is greater than that of galvinoxyl. This may be due to induced decomposition by the hydrazyl. Increasing concentrations of the hydrazyl fail to reduce the yield of carbon dioxide to zero. In the case of acetyl peroxide the yield levels off at about 40%. It is argued that this leveling-off is not explainable unless acetoxy radicals are being trapped by the hydrazyl. At low concentrations of acetyl peroxide and diphenylpicrylhydrazyl (near 10^{-4} M) trapping of the acetoxy radical occurs to a small extent, if at all. It appears that the problem of the decomposition of diacyl peroxides in the presence of diphenylpicrylhydrazyl needs to be resolved further. Experiments with both peroxides in solutions of cyclohexene containing 9,10-dihydroanthracene indicate that the acyloxy radicals prefer to add to the double bond rather than abstract allylic hydrogen. It is our view that the rates of decomposition of acetyl peroxide in cyclopentene and cyclohexene and the rates of formation of the cycloalkyl acetates together show the participation of the acetoxy radical in ester formation. Attempts to substantiate this point of view by scavenging the acetoxy radical have given results which are ambiguous.

The decomposition of acetyl peroxide in cyclohexene was shown to be unique[3] in that a substantial part of

the acetoxy groups of the peroxide was recovered as cyclohexyl acetate. The formation of the saturated ester was interpreted[3] as a radical addition reaction and
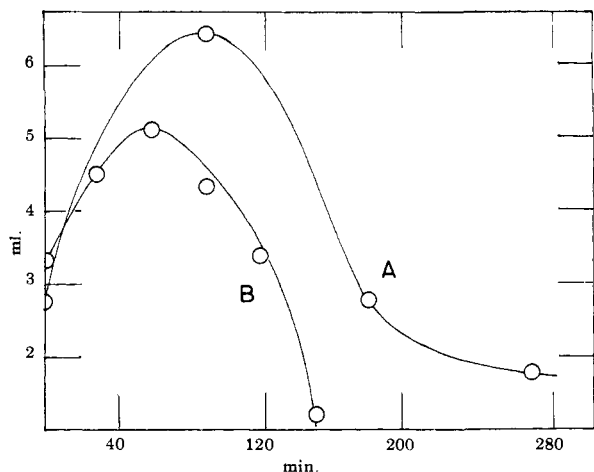
Fig. 1.—The decomposition of acetyl peroxide at 80° in mixtures of carbon tetrachloride and water. Plot of volume of 0.01 N sodium thiosulfate solution against time. Each point represents a sample tube containing 4 ml. of 0.05 M acetyl peroxide and (A) 1 ml. of water, (B) 0.5 ml. of water. The iodometric titrations were made on solutions at −20°.

Fig. 2.—The rate of decomposition of acetyl peroxide at 80°. Plots of log $(a − x)$ against time, where a and x are the initial and time t volumes of 0.01 N sodium thiosulfate used. Solvents were A, cyclohexene; B, cyclopentene; C, hexene-1.

was claimed as demonstrating the finite lifetime of the acetoxy radical. Later work by Martin and Drew[4] with labeled acetyl peroxide showed that part, if not all, of the cyclohexyl acetate was attributable not to an acetoxy radical reaction, but to a molecular reaction between acetyl peroxide and cyclohexene. Corroborative evidence used[4] in making this conclusion was the earlier report by Walling and Hodgdon[5] that the iodine–water technique,[6] when applied to acetyl peroxide, gave carbon dioxide (83%), methane, and methyl iodide, in contrast to benzoyl peroxide which gave almost quantitative conversion to benzoic acid. The use of iodine–water as a trapping system with acetyl peroxide was reinvestigated by Shine and Hoffman[7] and it was found that the evolution of carbon dioxide was markedly reduced. Thus, the data indicated that acetoxy radicals were being trapped in the iodine–water system. Subsequent work[8] showed that the iodine–water data were ambiguous, since acetyl peroxide, in contrast to benzoyl peroxide, was hydrolyzed rapidly by water alone. Therefore, the trapping of acetoxy radicals by this system was not a certainty, and hence, the distinction between a molecular and a radical path to cyclohexyl acetate was again unsettled.

We wish to report now our detailed results with the iodine–water system and with the trapping agents dihydroanthracene, diphenylpicrylhydrazyl, and galvinoxyl. We are also able to report our data on the rates of decomposition of acetyl peroxide in solution and on the rates of formation of saturated ester when this peroxide is decomposed in cyclopentene and cyclohexene.

Results

Kinetics.—The rate constants for the decomposition of acetyl peroxide in several solvents are given in Table I. In each case the disappearance of the peroxide followed first-order kinetics cleanly. It is noticeable that at a given temperature the rates of decomposition do not vary markedly from one solvent to another,

(4) J. C. Martin and E. H. Drew, J. Am. Chem. Soc., 83, 1234 (1961).

(5) C. Walling and R. B. Hodgdon, Jr., ibid., 80, 228(1958).

(6) G. S. Hammond and L. M. Soffer, ibid., 72, 4711 (1950).

(7) H. J. Shine and D. M. Hoffman, ibid., 83, 2782 (1961).

(8) H. J. Shine, J. A. Waters, and D. M. Hoffman, Abstracts, 140th National Meeting of the American Chemical Society, September, 1961, p. 72Q. The abstract does not contain the data on the effect of water, which were presented.
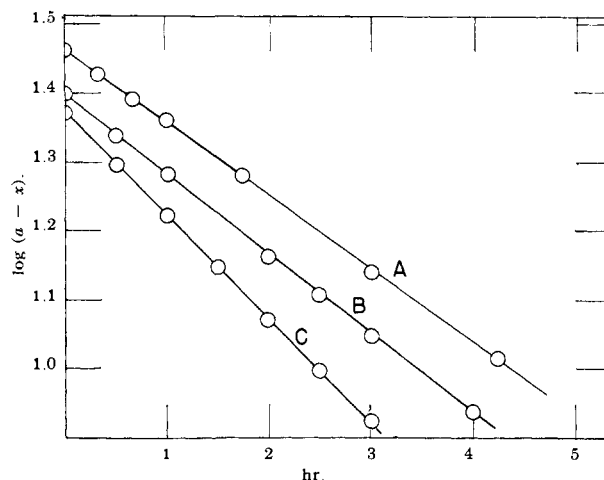
although there is a decrease in rates in going from pentene-1 through carbon tetrachloride. In particular, the rates of decomposition in cyclopentene and cyclohexene are very close. The presence of iodine lowers the rate of decomposition in carbon tetrachloride. The presence of 9,10-dihydroanthracene raises the rate of decomposition in this solvent, while, when in benzene solution, 9,10-dihydroanthracene causes a small decrease in the rate of decomposition. Decomposition in cumene is slower, but not markedly so, than in benzene. The addition of water to a carbon tetrachloride solution causes an increase in rate, the increase being greater the larger the water volume. During decomposition in the presence of water there was formed a product which was titratable at −20° by the iodometric method. The concentration of this product reached a maximum before all of the acetyl peroxide had decomposed and then decreased, as is shown in Fig. 1.

Energies of activation calculated from the data for four of the olefinic solvents in Table I in kcal./mole were: 2-methylpentene-1, 30.3; cyclohexene, 31.9; hexene-1, 31.7; and cyclopentene, 32.8.

Representative plots of log peroxide concentration against time are given in Fig. 2.

Rates of decomposition of benzoyl peroxide in benzene and cumene were measured for purposes of comparison and are given in Table II. The inclusion of 9,10-dihydroanthracene caused an increase in the rate of decomposition of this peroxide in benzene solution; this is the opposite of what was observed with acetyl peroxide.

In Table III are given the rates of formation of the saturated esters and the yields of esters formed from acetyl peroxide in the cycloolefins. Concentrations of the esters were determined with the use of temperature-programmed gas chromatography. The rates of formation of the saturated esters were obtained by plotting the concentration of saturated ester against $1 − e^{-kt}$. These plots are shown in Fig. 3. It can be seen from Table III that the rate of formation of cyclopentyl acetate is about twice as fast as that of cyclohexyl acetate, and also that the yield of the cyclopentyl ester is the larger.

Trapping Experiments.—The extent of "trapping" an acyloxy radical was measured in terms of the decrease in the formation of carbon dioxide when decomposition occurred in the presence of a radical trap. The radical traps used were iodine–water,

TABLE I

RATES OF DECOMPOSITION OF ACETYL PEROXIDE

Solvent	$10^2 \times M$, Ac₂O₂	Temp., °C.	$10^5 k$, sec.⁻¹	Solvent	$10^2 \times M$, Ac₂O₂	Temp., °C.	$10^5 k$, sec.⁻¹
Pent-1-ene	5.0	70	2.47	Cyclohexene	4.9	70	1.84
	5.0	70	2.43		5.0	70	1.71
	5.0	80	9.29		19.9	70	2.01
	5.0	80	9.54		4.8	80	7.06
	5.0	90	32.2		5.1	80	6.88
	5.0	90	32.3		10.2	80	7.10
2-Me-pent-1-ene	6.7	70	2.48		5.4	90	23.2
	5.1	80	9.25		5.0	90	22.4
	4.8	80	9.01		5.0	100	74.8
	4.8	90	31.2		5.0	100	77.5
	6.3	90	31.7	Cyclopentene	5.0	70	1.61
	4.8	100	98.1		4.9	70	1.59
Hex-1-ene	5.0	70	2.35		4.9	80	6.65
	4.9	70	2.33		5.0	80	7.34
	4.9	80	8.87		5.0	80	8.16
	5.0	80	8.73		5.0	90	25.5
	5.0	90	30.5		5.0	100	72.5
	4.9	90	30.0	CCl₄	5.1	80	5.59
	4.9	100	98.7		5.1	80	5.33
	5.0	100	98.3		5.0	80	5.66
Benzene	5.0	80	8.50		4.3	80	4.76[b]
	5.0	80	8.93		2.9	80	4.90[c]
	5.0	80	7.78[a]		4.0	80	9.29[d]
	5.0	80	6.50[a]		4.4	80	8.28[e]
Cumene	5.0	80	7.61		5.0	80	8.16[a]
	5.0	80	7.52		5.0	80	7.00[a]
Cyclohexene	4.5	60	0.448		5.0	80	6.92[a]
	12.4	60	0.451		5.0	80	8.42[a]
	17.9	60	0.447		5.0	80	5.47[f]
	20.0	60	0.487				

[a] 0.5 M 9,10-dihydroanthracene. [b] 0.041 M I₂. [c] 0.023 M I₂. [d] A 4-ml. sample containing 1 ml. of H₂O. [e] A 4-ml. sample containing 0.5 ml. of H₂O. [f] 0.5 M cumene.

TABLE II

RATES OF DECOMPOSITION OF BENZOYL PEROXIDE AT 80°

Solvent	$10^2 \times M$, Bz₂O₂	$10^5 k$, sec.⁻¹
Benzene	5.0	4.04
Benzene	5.0	4.12
Benzene	5.0	6.55[a]
Benzene	5.0	6.09[a]
Cumene	5.0	4.22
Cumene	5.0	4.18

[a] 0.5 M 9,10-dihydroanthracene.

TABLE III

RATES OF FORMATION AND YIELDS OF CYCLOALKYL ACETATES AT 80°

Solvent	Ester	$10^5 C$,[a] sec.⁻¹	%, Yield
Cyclohexene	Saturated	2.69	..
	Unsaturated	..	..
	Saturated	2.54	16.4
	Unsaturated	..	2.8
	Saturated	2.20	17.4
	Unsaturated	..	2.8
Cyclopentene	Saturated	5.77	..
	Unsaturated	..	..
	Saturated	5.19	31.4
	Unsaturated	..	2.1

[a] For a definition of C see later, under Discussion.

diphenylpicrylhydrazyl, galvinoxyl, and 9,10-dihydroanthracene. In the last case both the yield of carbon dioxide and of carboxylic acid were measured. Decomposition in cumene was also studied.

The effects of iodine and water on the decomposition of acetyl peroxide are given in Table IV. It is evident that water alone causes a large decrease in the carbon dioxide yield. It can be seen from Table V that the effect of water on the decomposition of benzoyl peroxide is in the same direction but not at all as severe. At constant water content increasing the iodine concen-
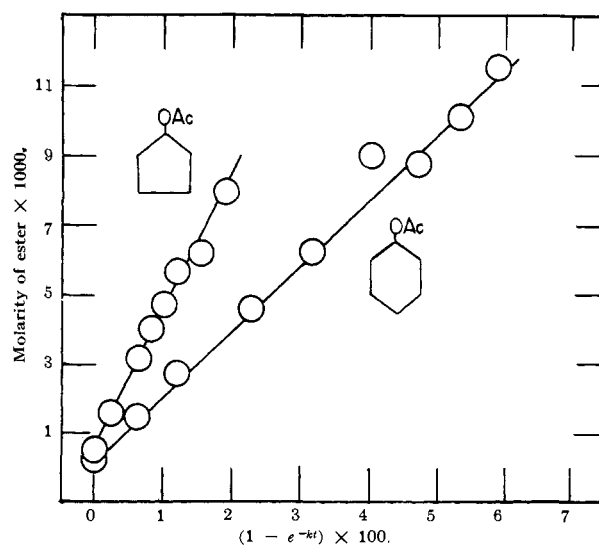

Fig. 3.—The rates of formation of cyclopentyl and cyclohexyl acetate from the decomposition of acetyl peroxide in cyclopentene and cyclohexene at 80°. Plots of ester concentration against $(1 - e^{-kt})$, where k is the averaged rate constant for the disappearance of acetyl peroxide in the appropriate olefin at 80°. The times t were in seconds.

tration relative to acetyl peroxide (Table IV) causes further decrease in the yield of carbon dioxide from the decomposition of the peroxide.

TABLE IV

THE EFFECT OF IODINE AND WATER ON THE DECOMPOSITION OF ACETYL PEROXIDE IN CARBON TETRACHLORIDE[a]

ml. soln.	$10^2 \times M.$ Ac$_2$O$_2$	$10^2 \times M.$ I$_2$	ml. H$_2$O	% CO$_2$	ml. soln.	$10^2 \times M.$ Ac$_2$O$_2$	$10^2 \times M,$ I$_2$	ml. H$_2$O	% CO$_2$
85	5.41	0.0	5	55.8	83	5.42	26.7	2	48.4
85	5.41	.0	5	55.1	83	5.27	26.7	2	49.1
85	5.41	.0	5	56.1	83	5.27	26.7	2	44.1
85	5.41	.0	5	54.0	83	5.27	26.7	2	48.9
85	5.41	.0	5	54.6	83	5.27	26.7	2	47.7
85	5.41	.0	5	56.0	75	5.0	31.5	2	45.1
85	5.42	.0	2	64.6	75	5.0	31.5	2	48.6
85	5.42	.0	2	63.3	85	5.18	54.4	2	40.1
85	5.42	.0	2	63.6	85	5.18	54.4	2	34.9
83	5.42	.0	2	65.3	85	5.18	54.4	2	40.2
83	5.42	.0	2	62.6	85	5.18	54.4	2	37.2
83	5.42	26.7	2	49.2	85	5.18	54.4	2	41.3
83	5.42	26.7	2	49.3	75	5.0	63.0	2	36.2

[a] At 80°.

TABLE V

THE EFFECT OF WATER ON THE DECOMPOSITION OF BENZOYL PEROXIDE IN CARBON TETRACHLORIDE[a]

$10^2 \times M,$ Bz$_2$O$_2$	ml. H$_2$O	CO$_2$, %	$10^2 \times M.$ Bz$_2$O$_2$	ml. H$_2$O	CO$_2$, %
5.45	2	97.9	5.68	5	95.1
5.45	2	98.1	5.68	5	95.7
5.45	2	97.9	5.68	5	94.7
5.45	2	97.7	5.68	5	95.8
5.45	2	97.9	5.68	5	96.7

[a] At 80°.

Results from the use of diphenylpicrylhydrazyl are given in Table VI, while those from using galvinoxyl are given in Table VII.

droxide, and the figures given in Table VIII are mole per cent titratable acid. They do not necessarily mean titratable carboxylic acid, as will be discussed later. That the effect of 9,10-dihydroanthracene varies with the solvent is immediately evident. In carbon tetrachloride solution it might appear that 9,10-dihydroanthracene traps the acetoxy radical, giving rise to a large amount of acid and a corresponding drop in carbon dioxide. Comparison with the results in benzene solution shows, however, that this effect of the 9,10-dihydroanthracene is not observable. When benzoyl peroxide is decomposed in benzene solutions containing 9,10-dihydroanthracene the carbon dioxide yield is lowered and a large rise in acid content is measured. Benzoyl peroxide in carbon tetrachloride alone gives rise to a sizable acid content. In solutions of carbon tetrachloride containing 9,10-dihydroanthracene the fall in carbon dioxide and the rise in acid are much larger than observed in similar benzene solutions.

Solutions of cyclohexene containing 9,10-dihydroanthracene give the most interesting results. The 9,10-dihydroanthracene causes not only no significant change in the products from acetyl peroxide, but also affects the decomposition of benzoyl peroxide to only a small extent. That is, in each case the yield of carbon dioxide is virtually unaffected. The yield of acid from acetyl peroxide is not changed, while that from benzoyl peroxide increases by no more than 50% of what it was in the absence of the 9,10-dihydroanthracene.

Finally, in Table IX are given the data from decomposition in cumene. Here, it can be seen that, as might be expected, the carbon dioxide yield from benzoyl peroxide is lowered while that from acetyl peroxide is as high as obtained from decomposition in benzene and carbon tetrachloride (Table VIII).

TABLE VI

THE DECOMPOSITION OF ACETYL AND BENZOYL PEROXIDES IN BENZENE SOLUTIONS CONTAINING DIPHENYLPICRYLHYDRAZYL

Peroxide	$M \times 10^4$	DPPH, $M \times 10^4$	CO$_2$, %	Temp., °C.	Peroxide	$M \times 10^4$	DPPH, $M \times 10^4$	CO$_2$, %	Temp., °C.
Acetyl	400	800	53.4	80	Acetyl	1.8	3.5	88.0	70
	380	..	82.2	80		1.8	3.5	84.2	70
	380	..	85.3	80		1.8	....	93.2	70
	380	..	88.6	80		2.1	3.5	85.9	70
	380	..	84.3	80		2.1	....	94.5	70
	380	950	55.2	80	Benzoyl	490	....	81.3	80
	380	950	54.3	80		490	....	79.5	80
	380	1900	50.2	80		490	....	78.8	80
	380	1900	49.1	80		490	1510	2.4	80
	380	1900	49.5	80		490	1510	3.1	80
	380	2850	43.8	80		490	3020	3.0	80
	380	2850	43.6	80		490	4530	2.8	80
	380	3800	39.7	80		490	6040	4.3	80
	380	3800	41.2	80		1.5	3	62.0	70
	380	3800	39.5	80		1.5	....	90.8	70
	1.5	..	100	70		1.5	....	93.0	70

Here it can be seen that the presence of the trapping agent causes a decrease in the yield of carbon dioxide. Table VI shows that the decrease in the carbon dioxide yield depends not only on the relative concentrations of peroxide and diphenylpicrylhydrazyl but also on their absolute concentrations. Thus, a 100% excess of the hydrazyl in a 4×10^{-2} M solution of peroxide causes a large drop in the yield of carbon dioxide, whereas a similar excess in 1.8×10^{-4} M peroxide caused a decrease of 5–10%.

In Table VIII are assembled the results of adding 9,10-dihydroanthracene to solutions in which the peroxides were decomposing.

The carbon dioxide and acid yields are listed. The acid was determined by titration with sodium hy-

Discussion

Rates of Decomposition and Ester Formation.—The rates of decomposition of acetyl peroxide in the solvents listed in Table I are not characterized by any particularly marked solvent effects. There is a trend toward lower rates in going from pentene-1 through carbon tetrachloride but it is not large. The small difference between benzene and carbon tetrachloride reported here is seen in other data for the two solvents collected by Walling.[9] The energies of activation of decomposition in the olefins are also very close and similar to those reported[9] for other solvents. Thus, it does not appear that decomposition in olefin solvents

(9) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 492.
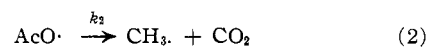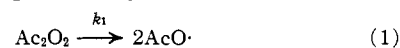
TABLE VII

THE DECOMPOSITION OF ACETYL AND BENZOYL PEROXIDES IN BENZENE SOLUTIONS CONTAINING GALVINOXYL AT 80°

Peroxide	Galvinoxyl, mole/l.	CO_2, %
Acetyl[a]	0.089	82.3
	.089	81.9
	.178	80.7
	.267	76.5
	.356	73.3
	...	89.7
	...	88.2
Benzoyl[b]	.059	22.5
	.059	21.4
	.118	10.6
	.178	7.5
	.237	7.0
	...	82.6
	...	81.0

[a] 0.049 M. [b] 0.048 M.

rates of peroxide decomposition in the two solvents are almost the same, the rates of formation of the saturated ester are not. The faster rate of formation of the cyclopentyl ester may be interpreted as analogous to either known cases of radical addition to these olefins[10] or to known cases of molecular reaction leading to addition.[11] Although the kinetic data do not permit the making of a clear-cut distinction between these two processes, it is possible to make some interesting observations that favor the radical addition step.

Let us list all of the processes of importance that are or may be occurring in the cycloolefin solutions. We

$$Ac_2O_2 \xrightarrow{k_1} 2AcO\cdot \qquad (1)$$

$$AcO\cdot \xrightarrow{k_2} CH_3\cdot + CO_2 \qquad (2)$$

have omitted reactions of induced decomposition and also the bimolecular reactions of acetyl peroxide that lead to methyl acetate since they do not add to or detract from the argument that follows.

TABLE VIII

THE DECOMPOSITION OF ACETYL AND BENZOYL PEROXIDES IN THE PRESENCE OF 9,10-DIHYDROANTHRACENE

Peroxide and solvent	$10^2 \times M$, peroxide	$10 \times M$, DHA	CO_2, %	Acid, %	Peroxide and solvent	$10^2 \times M$, peroxide	$10 \times M$, DHA	CO_2, %	Acid, %
Ac_2O_2 CCl_4	5.0	4.87	72.5	16.9	Ac_2O_2	4.7	5.0	64.0	6.1
	5.0	4.87	64.4	25.3	cyclohexene	4.7	5.0	64.3	3.9
	5.0	0.0	87.0	0.9	Bz_2O_2	5.5	5.0	4.6	17.6
	5.5	4.75	47.9	48.0	cyclohexene	5.5	5.0	3.9	20.2
	5.5	4.75	45.8	47.6		5.5	5.0	4.2	17.3
	5.5	4.75	47.1	44.7		5.5	0.0	4.2	12.2
	5.5	0.0	87.1	0.7		5.5	0.0	4.5	11.9
	5.5	.0	88.4	1.0		5.5	0.0	4.0	12.6
	5.5	.0	87.1	0.8		4.9	2.08	5.7	13.8
	6.5	4.87	39.3	53.0		4.9	0.0	4.0	12.4
	6.5	4.87	58.7	35.0		4.9	0.0	4.1	12.2
	6.5	0.0	90.3	0.5	Ac_2O_2 benzene	6.0	4.77	82.1	3.5
Bz_2O_2 CCl_4	4.5	2.08	35.5	56.3		6.0	4.77	81.2	4.4
	4.5	2.08	37.6	53.4		6.0	0.0	84.6	2.8
	4.5	0.0	93.7	22.0		6.0	0.0	84.3	3.0
	4.9	4.77	18.5	71.0		6.0	0.0	84.8	3.2
	4.9	4.77	18.9	69.0	Bz_2O_2 benzene	4.6	5.2	36.6	56.0
	4.9	4.77	18.9	73.3		4.6	5.2	36.7	54.9
	4.9	0.0	92.2	24.0		4.6	5.2	36.7	54.5
	4.9	0.0	91.6	23.4		4.6	0.0	87.0	11.6
Ac_2O_2	5.3	2.08	68.5	4.0		4.6	0.0	86.5	11.2
cyclohexene	5.3	0.0	67.6	3.5		4.6	0.0	86.0	11.9
	5.3	0.0	68.4	..					

TABLE IX

THE DECOMPOSITION OF ACETYL AND BENZOYL PEROXIDES IN CUMENE SOLUTION AT 80°

Peroxide	CO_2, %	Acid, %
Acetyl[a]	85.8	1.6
	85.4	1.5
	84.9	1.4
Benzoyl[b]	68.4	20.8
	66.7	19.7
	67.6	19.6
	69.2	19.5
	69.4	20.0
	66.8	20.6

[a] 0.064 M. [b] 0.05 M.

is associated with any process different from decomposition in, say, benzene or carbon tetrachloride, and large enough in extent to markedly affect the rate of decomposition of the peroxide. In particular, the rates of decomposition in cyclopentene and cyclohexene are hardly distinguishable from each other. Decomposition in these solvents leads to the formation of the saturated and unsaturated esters, and, whereas the over-all

$$(3)$$

$$(4)$$

$$(5)$$
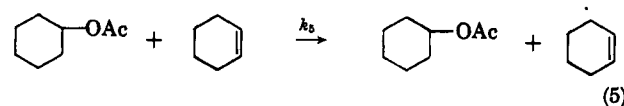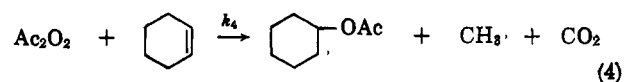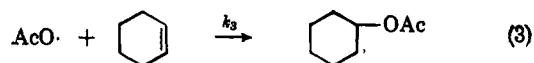
By assuming steady state concentrations of the radicals AcO· and $[C_6H_{10}-OAc]\cdot$ it is possible to derive the expression

$$\frac{dE}{dt} = \left\{ \frac{2k_1k_3[S]}{k_3[S] + k_2} + k_4[S] \right\} A \qquad (6)$$

for the rate of formation of the saturated ester (E) in terms of the concentration of the peroxide A, the

(10) M. S. Kharasch and H. N. Friedlander, J. Org. Chem., **14**, 239 (1949); E. S. Huyser, ibid., **26**, 3261 (1961); J. Gresser, A. Rajbenbach, and M. Szwarc, J. Am. Chem. Soc., **83**, 3005 (1961).

(11) K. Ziegler and H. Froitzheim-Kühlhorn, Ann., **589**, 157 (1954); H. C. Brown and A. W. Moerikofer, J. Am. Chem. Soc., **83**, 3417 (1961).

rate constants shown in eq. 1 through 5, and the concentration of the solvent (cycloolefin), S.

This equation may be written

$$\frac{dE}{dt} = CA_0 e^{-kt} \tag{7}$$

where C depicts all of the constants in eq. 6, A_0 is the initial concentration of peroxide, and k the rate constant of over-all loss of peroxide. Integration gives

$$E = \frac{CA_0}{k}(1 - e^{-kt}) \tag{8}$$

from which it can be seen that plotting E against $(1 - e^{-kt})$ will give a straight line, which is what we have done in determining the rates of formation of the ester. The slope of this line is CA_0/k and it is this that we are using for comparison in the case of the two olefins. Our values for the rate constant k, which describes the over-all disappearance of peroxide, are about the same for the two cycloolefins. Therefore, the difference in rates of ester formation given in Table III depends on C, where

$$C = \left\{ \frac{2k_1k_3[S]}{k_3[S] + k_2} + k_4[S] \right\}$$

It is unlikely that k_1, which describes the purely thermal scission of the peroxide, will be different for the two cycloolefins. The value of [S] is 9.9 for cyclohexene and 11.3 for cyclopentene, a difference that is not going to affect C much. Therefore, if, as is probable, k_2 is appreciably larger than k_3, the value of C is directly dependent on k_3 and k_4.

The peroxide is shown in eq. 1–5 to disappear by two processes so that the rate constant for the over-all loss of peroxide, neglecting induced decompositions, is

$$k = k_1 + k_4[S]$$

It is to be expected that, if the reaction 4 occurs, the values of k_4 for the two cycloolefins should differ. Since our values for k at several temperatures indicate that the peroxide disappears in cyclopentene at about the same rate as in cyclohexene, we must conclude that k_4 is either zero in each case or is too small to be detected within our limits of experimental error. Therefore, the indications are that the difference between values of C for cyclopentene and cyclohexene are due to differences in k_3.

Thus, it is deduced that the kinetic data indicate that the rate of disappearance of the peroxide is the rate at which it undergoes unimolecular homolysis, while the difference in rates of saturated ester formation reflect the already well documented difference with which radicals add to the two cycloolefins.

It is interesting to note that Lamb and his collaborators[12] have recently ruled out a molecular collision reaction between cyclohexene and δ-phenylvaleryl peroxide.

Iodine and Water.—Iodine lowers slightly the rate of decomposition of acetyl peroxide in carbon tetrachloride solution. This is undoubtedly due to the prevention by iodine of some radical-caused induced decomposition.

The rate of decomposition of acetyl peroxide in mixtures of carbon tetrachloride and water is faster than in dry carbon tetrachloride and becomes faster as the ratio of water to carbon tetrachloride is raised. This is an important observation view of our earlier claim[7] that the iodine–water technique appeared to trap the acetoxy radical. The effect of the water is no doubt mainly in the hydrolysis of the peroxide. The hydrolysis should lead to acetic and peracetic acids.

The peracid is more easily reduced by iodide, and therefore can be titrated at a lower temperature[13] than the acyl peroxide. We were, therefore, able to follow the hydrolysis of the peroxide by titrating the peracetic acid formed at $-20°$, at which temperature acetyl peroxide is only slowly reduced. The peracetic acid concentration reached a maximum and then decreased indicating that it was forming at a measurably rapid rate and decomposing subsequently more slowly. The rate constants for the decomposition of the peroxide in the aqueous systems are the sum of rate constants for the two processes, loss by hydrolysis, and thermal homolysis. First-order kinetics were followed nicely, however, and no attempt was made to carry the kinetic analysis further.

The effect of water in the hydrolysis of acetyl peroxide results also in the loss of carbon dioxide. Data given in Table IV show that this loss can be measured reproducibly. Benzoyl peroxide undergoes a similar reaction as shown in Table V, and here the comparatively very small effect of the water is probably due partly to the lower solubility of the benzoyl peroxide in water.

In view of the hydrolysis by water and our earlier report[7] the use of iodine–water mixtures was again investigated. At constant water volume increasing iodine concentrations caused increasing losses in carbon dioxide. Although the addition of iodine gave the results in Table IV it is not certain that the fall in carbon dioxide is due to trapping by iodine rather than to reduction by the hydrogen iodide formed by hydrolysis of the iodine. This ambiguity is now to be expected in all cases of easily hydrolyzable peroxides. Also, where the effect of iodine–water on a peroxide of low water solubility is small[14] this effect may be due to hydrolysis rather than trapping.

Diphenylpicrylhydrazyl.—This compound has been used by other workers in studies of the decomposition of diacyl peroxides. Barson and Bevington[15] have shown that the yield of carbon dioxide from the decomposition of benzoyl peroxide in benzene is lowered by the presence of the hydrazyl. The yield of carbon dioxide approached zero as the concentration of the hydrazyl was increased, although, even with a large excess of hydrazyl, some carbon dioxide was still formed.

Kinetic studies with diphenylpicrylhydrazyl and the decomposition of acetyl,[16] lauroyl,[16,17] and benzoyl[18] peroxides have shown that the rate step in each case is the scission of the peroxide and does not involve the hydrazyl, although the method of kinetic analysis does not distinguish between acyloxy and alkyl (or aryl) radical capture by the hydrazyl. The kinetic studies of pertinence to this discussion are those of Bawn.[16,18] In these studies the concentrations of reactants were very low (in the region of 10^{-5} and 10^{-4} M) and, for the most part, the concentration of peroxide was greater than that of the hydrazyl. It was shown, however, with both acetyl and benzoyl peroxides, that even when the hydrazyl was in 100% excess the same kinetic features held.

Our work with acetyl peroxide (Table VI) shows that in concentrations near 10^{-2} M a large drop in carbon dioxide is caused by 100% excess of diphenylpicrylhy-

(12) R. C. Lamb, F. F. Rogers, Jr., G. C. Dean, Jr., and F. W. Voight, Jr., *J. Am. Chem. Soc.*, **84**, 2635 (1962).

(13) F. Fichter and R. Zumbrunn, *Helv. Chim. Acta*, **10**, 869 (1927), for example, with percaproic acid and caproyl peroxide.

(14) D. F. DeTar and R. C. Lamb, *J. Am. Chem. Soc.*, **81**, 122 (1959).

(15) C. A. Barson and J. C. Bevington, *J. Polymer Sci.*, **20**, 133 (1956).

(16) C. E. H. Bawn and R. G. Halford, *Trans. Faraday Soc.*, **51**, 780 (1955).

(17) V. Vorobiev, D. Lefort, J. Sorba, and D. Rouillard, *Bull. Soc. Chim. France*, 1577 (1962).

(18) C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).

drazyl. Thereafter, increasing the initial concentrations of the hydrazyl does not cause further large decreases in carbon dioxide yield. On the other hand in concentrations near 10^{-4} M, that is, approaching the range of concentrations used by Bawn, a 100% excess of the hydrazyl causes only a very small fall in the carbon dioxide yield. The same features are to be seen in our results with benzoyl peroxide. In this case the fall in carbon dioxide yield caused by 100% excess diphenylpicrylhydrazyl in the 10^{-4} M range is still large.

The decrease in carbon dioxide observed in the presence of diphenylpicrylhydrazyl may be attributed to two causes: induced decomposition by attack of the hydrazyl on the peroxide; and trapping of the acyloxy radical. Bawn has been able to exclude the induced decomposition at low concentrations. Trapping of acyloxy radicals at these concentrations, however, is not complete unless a large excess of the hydrazyl is present. Thus, Barson and Bevington's data show that, with 2×10^{-3} M benzoyl peroxide, even a 15-fold excess of the hydrazyl gave a 10% yield of carbon dioxide, while a 200% excess of the hydrazyl gave a 37% yield of carbon dioxide. Even with these data, in spite of the low concentrations, it is still not possible to say with certainty that trapping efficiency is at a maximum and induced decomposition is absent. Keeping Bawn's work in mind it seems reasonably safe to conclude that lowered carbon dioxide yields indicate that trapping of acyloxy radicals is occurring in solutions of low concentration and where the hydrazyl is in 100% excess. This would mean, in our case, that the evidence for trapping the acetoxy radical is only very slender. At the high concentrations, where our carbon dioxide yields drop markedly, induced decomposition may account for much of the fall. The yield of carbon dioxide from 3.8×10^{-2} M solutions of acetyl peroxide levels off at about 40%. There are several possible ways of explaining a leveling-off in carbon dioxide. Induced decomposition by collision with diphenylpicrylhydrazyl may cause the capture of one acetoxy portion and the simultaneous or subsequent rupture of the second into methyl and carbon dioxide. In this case the leveling-off at 40% carbon dioxide requires that 80% of the acetyl peroxide is involved in this type of collision. This in turn requires that 20% of the peroxide disappears by a route that does not lead to carbon dioxide. The routes available are acetoxy radical trapping or methyl acetate formation. Edwards and Mayo[19] have shown that in carbon tetrachloride at 76°, 16% of decomposing acetyl peroxide goes to methyl acetate, while Szwarc[20] has shown that in isooctane at 65° about 20% goes to methyl acetate, and, furthermore, by "cage" reaction. But, these methyl acetate formations must lead to carbon dioxide formation, too; 8 and 10%, respectively, of the theoretically available. Thus, in our case, the 20% peroxide to be accounted for, if 80% of the peroxide is removed by collision with the hydrazyl, cannot be going to methyl acetate. Looked at in another way, if about 20% of the peroxide does undergo "cage" decomposition to give methyl acetate (and a 10% yield of carbon dioxide), only 60% of the peroxide can be removed by the type of hydrazyl-induced decomposition described, giving a 30% yield of carbon dioxide.

In fact, there is no way of accounting for all of the acetyl peroxide on the basis of this type of hydrazyl-induced decomposition.

Second, the leveling-off of the carbon dioxide at 40% may represent the portion of the peroxide which decomposes by routes unaffected or unapproachable by

the hydrazyl. If we include among these routes the estimate of methyl acetate "cage" formation, we have a maximum of 50% of the peroxide decomposing by these "unapproachable" routes. This leaves 50% of the peroxide available for attack by the hydrazyl by a route that cannot lead to carbon dioxide.

It is apparent that the difficulty in accounting for all of the acetyl peroxide is removed if the diphenylpicrylhydrazyl is actually trapping acetoxy radicals. In this case the acetoxy radicals can be formed by scission of acetyl peroxide or by hydrazyl-induced decomposition leading to an intact acetoxy radical that is trappable. If this is the case, our data at the low concentrations would reflect the same problem that Barson and Bevington encountered with benzoyl peroxide; that is, in having enough hydrazyl available to capture benzoate radicals.

Galvinoxyl.—This stable radical has not been used as extensively as diphenylpicrylhydrazyl in trapping experiments. Martin[21] found that the efficiency of galvinoxyl was greater than that of diphenylpicrylhydrazyl in perester decompositions. Bartlett[22] found that galvinoxyl was more efficient than iodine toward the 2-cyan-2-propyl radical. Our results with diphenylpicrylhydrazyl and galvinoxyl might be taken as showing that the hydrazyl is the more efficient trapping agent. The large difference between the effects of 100% excess galvinoxyl (82% carbon dioxide) and 100% diphenylpicrylhydrazyl (53% carbon dioxide) is probably due to induced decomposition by the hydrazyl. Induced decomposition by galvinoxyl cannot be ruled out, and it is questionable whether our results with this compound are to be attributed to trapping or induced decomposition. While it is our feeling that, in the case of acetyl peroxide, the slow fall in the carbon dioxide yield to only 73% as the galvinoxyl concentration is increased fourfold points more to trapping than induced decomposition, the question of trapping vs. induced decomposition in diacyl peroxides needs to be resolved.

9,10-Dihydroanthracene.—Decomposition of both peroxides in carbon tetrachloride solutions of 9,10-dihydroanthracene gave erratic results. The high yield of acidic products in addition to the large yield of carbon dioxide obtained from benzoyl peroxide alone in carbon tetrachloride is understandable on the basis of the work of Boeseken and Gelissen.[23] The decomposition of acetyl peroxide alone in carbon tetrachloride is quite clean. The large change in acidic products observed when 9,10-dihydroanthracene is added to the acetyl peroxide solutions (Table VIII) must be attributed to reactions involving carbon tetrachloride and 9,10-dihydroanthracene. It is possible that the dihydroanthracenyl radical abstracts a chlorine atom from carbon tetrachloride and that the so formed 9-chloro-9,10-dihydroanthracene undergoes thermal loss of hydrogen chloride. The two peroxides were evidently subjected to the same side reactions. The increased rate of decomposition (Table I) of acetyl peroxide in carbon tetrachloride solutions of 9,10-dihydroanthracene is no doubt also due to reaction with products such as hydrogen chloride.

In contrast, the lowering of the rate of decomposition of acetyl peroxide caused by 9,10-dihydroanthracene in benzene (Table I) is attributable to the suppressing of some induced decomposition. At the same time, the changes in yield of carbon dioxide and acid (Table VIII) are too small to be attributed with reliability to hydrogen abstraction.

(19) F. G. Edwards and F. R. Mayo, *J. Am. Chem. Soc.*, **72**, 1265 (1950).
(20) L. Herk, M. Feld, and M. Szwarc, *ibid.*, **83**, 2998 (1961).
(21) W. G. Bentrude and J. C. Martin, *ibid.*, **84**, 1561 (1962).
(22) P. D. Bartlett and T. Funahashi, *ibid.*, **84**, 2596 (1962).
(23) J. Boeseken and H. Gelissen, *Rec. trav. chim.*, **43**, 869 (1924).

Benzoyl peroxide in benzene containing 9,10-dihydroanthracene gives rise not only to less carbon dioxide and more acid, but here the rate of decomposition is increased. The increased rate of decomposition may be attributed to either a change in medium, to which this peroxide is very sensitive,[24] due to the formation of benzoic acid during decomposition, or to induced decomposition by dihydroanthracenyl radicals. These carbon dioxide and acid data (Table VIII) illustrate again the well known differences in behavior of the two peroxides.

The results obtained with the two peroxides in cyclohexene solutions of 9,10-dihydroanthracene are of interest, particularly those with benzoyl peroxide. The concentration of the 9,10-dihydroanthracene used, $5 \times 10^{-2} M$, is about one-twentieth that of the solvent cyclohexene. On the other hand, Kooyman[25] has shown that toward the trichloromethyl radical, 9,10-dihydroanthracene is about 30 times more effective than cyclohexene as a hydrogen donor. It is apparent from the small yield of acid (about 12%) obtained from cyclohexene alone that benzoyloxy radicals do not abstract hydrogen readily from the allylic position of the olefin. Products of reaction of benzoyl peroxide with cyclohexene also show this.[26] A major product is reported to be cyclohexyl benzoate. When 9,10-dihydroanthracene is used in cyclohexene, the hydrogen abstraction reaction is increased by only an additional 6 to 8% (Table VIII). Yet benzoyloxy radicals are not unreactive in abstracting hydrogen from this donor, as is seen with benzene solutions. Whether 9,10-dihydroanthracene is used or not in the cyclohexene case, the yield of carbon dioxide is very low; in fact, it is about as low as can be obtained from benzoyl peroxide in the presence of the most effective traps. It is evident therefore that *the benzoyloxy radicals preferentially add to the olefinic linkage rather than abstract hydrogen.* An identical conclusion was recently reached by Kochi[27] from reactions with butenes.

When the case of acetyl peroxide is examined (Table VIII), one finds an indication of a fall in carbon dioxide and, possibly, a small increase in acid. Once again, with acetyl peroxide, the differences are too small to be used in argument, but, the results with benzoyl peroxide now add light to the decomposition of acetyl peroxide in cyclohexene, and also in other olefins. That is, there is every reason to believe that acetoxy radicals will add preferentially to the olefinic linkage. Indeed, it is probable that acyloxy radicals, in general, prefer to add to the olefinic linkage. These results show why very little acetic acid has been detected in cyclohexene solutions in previous work where the acetoxy radical has been proposed as a real reactant.[3]

Szwarc[20] has found no evidence for the addition of acetoxy radicals to styrene in isooctane solution, and has concluded that, since methyl radicals add 800 times faster to styrene than to cyclohexene, the absence of acetoxy radical addition to the styrene argues against the addition to cyclohexene. This argument needs further inspection, however, since in the cyclohexene experiments the solvent was neat cyclohexene while in the styrene it was a maximum of 7 mole % styrene in isooctane. The addition to cyclohexene may occur as a reaction with the solvent "cage," and we do not know what the precise environment of the peroxide is in the isooctane solutions. Further, it is not known whether acyloxy radicals show the same order of affinities to olefins as methyl radicals.

Experimental

Materials.—The olefins and cumene were Phillips pure grade. Prior to use they were passed through a column of silica gel (Davison, No. 950, 60–200 mesh). Benzene and carbon tetrachloride were reagent grade and were dried and distilled before use. The benzene was also passed through a column of silica gel. The 9,10-dihydroanthracene was from Aldrich Chemical Co., and was recrystallized from ethanol, m.p. 110–110.5°. Diphenylpicrylhydrazyl was prepared by the method of Goldschmidt and Renn,[28] and was recrystallized from chloroform. Benzoyl peroxide was from Monomer-Polymer Laboratories, Borden Chemical Co., and was purified by precipitation from chloroform by methanol. Acetyl peroxide was prepared by a modification of Gambarjan's method.[29-31] Galvinoxyl was prepared as described by Kharasch and Joshi.[32] Cyclopentyl acetate was prepared from cyclopentanol and had b.p. 147° (670 mm.). 3-Acetoxycyclopentene was prepared from 3-chlorocyclopentene and sodium acetate in acetic acid and had b.p. 54–55° (16 mm.). The 3-chlorocyclopentene was prepared by the method of Alder and Flock.[33] Cyclohexyl acetate was from Distillation Products and was distilled prior to use. 3-Acetoxycyclohexene was prepared from 3-bromocyclohexene as before and had b.p. 56–58° (65 mm.). The 3-bromocyclohexene was prepared from cyclohexene and N-bromosuccinimide.[34]

Kinetics.—A solution of peroxide was prepared and analyzed as described earlier.[7] The solution was diluted to the appropriate concentration and aliquots were pipetted into sample tubes capable of being attached to an oil diffusion-pump vacuum line. Where water was added it was pipetted directly into the sample tube. Iodine and 9,10-dihydrolanthracene were added as solutions of known concentration. The sample tubes were de-gassed by several cycles of the customary freezing and thawing technique using either liquid air or Dry Ice where appropriate. The tubes were immersed in a thermostated bath, removed at appropriate intervals, and the contents were analyzed for peroxide content. The tubes containing water were shaken continuously along a horizontal axis while in the bath. For the determination of peracetic acid in the water experiments the tube contents were titrated at −20°. The total peroxide content was determined[7] with a second tube removed at the same time. Rates of disappearance of peroxide were obtained from plots of log peroxide concentration against time. The values of the first-order rate constants given in Table I were obtained, however, by least mean squares calculations.[35] Activation energies for the decomposition of acetyl peroxide in some solvents were calculated also by this method.

For determining the rates of formation of cyclopentyl acetate and cyclohexyl acetate the concentration of the saturated ester at time intervals was determined from the area under the appropriate peak in the gas chromatogram. The sample for injection into the gas chromatograph was prepared as follows. After removal of the sample tube, containing 5 ml. of solution, from the bath at 80°, it was cooled in Dry Ice-ethanol slurry and opened. The contents were decanted into a 25-ml. standard taper flask containing a small amount of Dry Ice, and to this was added 1 ml. of a solution 0.5 M in potassium iodide and 0.001 M in acetic acid. The solution was stirred magnetically while boiling under reflux gently for 10 min. It was then cooled and stirred 1 min. with 2 ml. of 0.5 M sodium thiosulfate. The organic layer was separated under nitrogen, washed twice with 2-ml. portions of water, and dried over magnesium sulfate. Analysis for ester content was carried out with a 100-µl. sample on a 12-ft. column of LAC-728 on Gas-Chrom.-S. The chromatograph was an F and M Scientific Co. Model 300.

The rate of formation of saturated ester at 80° was calculated in the following way. The areas under the saturated ester peaks at times t were plotted against $(1 - e^{-kt})$, where k was the average value of the rate constants (Table I) for the disappearance of peroxide in the appropriate olefin at 80°. The slope of this plot was converted to concentration units by using a pre-determined calibration factor relating areas to molarity of the appropriate ester. This slope was then multiplied by k/A_0, the value of k being that described before, and A_0 the initial concentration of peroxide. The data given in Fig. 3 have been converted from areas to ester molarities for convenience.[36]

(24) Ref. 9, p. 478.
(25) Ref. 9, p. 264.
(26) P. H. Hermans and T. Van Eyk, *J. Polymer Sci.*, **1**, 407 (1946).
(27) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 1572 (1962).

(28) S. Goldschmidt and K. Renn, *Ber.*, **55**, 628 (1922).
(29) S. Gambarjan, *ibid.*, **42**, 4010 (1909).
(30) D. A. Shirley, "Preparation of Organic Intermediates," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 1.
(31) The modification of this method reported by J. R. Slagle and H. J. Shine, *J. Org. Chem.*, **24**, 107 (1959), while giving consistent results does not give, as claimed, higher yields than that reported by Shirley.[30]
(32) M. S. Karasch and B. S. Joshi, *ibid.*, **22**, 1435 (1957).
(33) K. Alder and F. H. Flock, *Ber.*, **89**, 1732 (1956).
(34) K. Ziegler, *Ann.*, **551**, 110 (1942).
(35) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand and Co., Inc., 6th printing, 1949, p. 502.
(36) The equation (8), $E = CA_0(1 - e^{-kt})/k$, from which these plots were

Yields of the saturated $(E\infty)$ and unsaturated ester were determined on samples in which peroxide decomposition was complete.

Carbon Dioxide and Acid Yields.—The appropriate solutions were prepared and degassed in flasks constructed to allow later sweeping with nitrogen by breaking sealed-tip side arms. The flasks were immersed in a thermostated bath at 80°, and remained for 48–50 hr. Where water had been added, the flask

made, can be written $E = C(A_0 - A)/k$. As $t \to \infty, A \to 0$, so that $E\infty = CA_0/k$. Substituting this expression for CA_0/k into eq. 8 gives $E = E\infty(1 - e^{-kt})$ which can be expressed in logarithmic form as $\ln (E\infty - E) = -kt + \ln E\infty$. Thus, a plot of $\ln (E\infty - E)$ against t should give k, the rate constant for disappearance of peroxide. We wish to acknowledge and thank Dr. Robert C. Lamb for calling this feature to our attention. We have plotted $\log (E\infty - E)$ against t for the two runs in cyclohexene and one run in cyclopentene for which $E\infty$ was known. The results were, for cyclohexene, $k = 6.93$ and 8.41×10^{-4} sec.$^{-1}$, and for cyclopentene, $k = 8.1 \times 10^{-5}$ sec.$^{-1}$. Considering the fact that values of E were obtained from peak areas after a somewhat cumbersome work-up procedure, these values of k are in fairly good agreement with those obtained by direct measurement and given in Table I.

was shaken vigorously during the whole of the heating period in a bath constructed for this purpose. Earlier it was found that magnetic stirring of the sealed contents did not give reproducible results. The flask was cooled and placed in the nitrogen sweep train. The nitrogen was passed through a bed of solid sodium hydroxide before entering the flask. After breaking the tips of the flask side arms, the carbon dioxide was swept out through a Dry Ice trap, concentrated sulfuric acid, quinoline, magnesium perchlorate, and into an Ascarite tube. The nitrogen sweep was continued until the Ascarite tube no longer gained weight. This time period also included finally allowing the Dry Ice trap to warm to 0°.

The acid content was determined by titrating all or part of the flask contents. The per cent acid listed in the tables refers to the appropriate carboxylic acid equivalent to the standard base used, and does not distinguish between HCl and carboxylic acid if the former was present (i.e., in carbon tetrachloride experiments).

Steric Effects on the Near-Ultraviolet Absorption (Soret Band) of Porphyrins[1]

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Earlier observers recorded that the formation of an octahedral complex of a metalloporphyrin with a nitrogenous base caused the appearance of a new absorption peak in the near-ultraviolet (Soret) region with a shift from a maximum at 390–400 mμ to one at 410–420 mμ. This effect is now ascribed to steric interference between the ligand and the π-electron system of the porphyrin ring, similar to that observed upon N-methylation. The same phenomenon occurring with the alkali metals and with Ag^1 is ascribed to the interferences between alkali metal atoms above and below the ring and the porphyrin π-electron system.

The coordination of iron porphyrins with bases has been studied by many investigators,[1,4] primarily because of the importance of these complexes with respect to the chemistry of hemoglobin. Miller and Dorough[5] showed, through a study of visible spectra, that magnesium, zinc, cadmium, mercury, copper, and cobalt porphyrins also form pyridinate complexes comparable in some respects to those formed by iron porphyrins. Erdman, Ramsey, Kalenda, and Hanson[6] extended the observation to vanadyl complexes and pointed out that complexing of the metalloporphyrin with pyridine caused the formation of a second near ultraviolet (Soret) peak at a longer wave length. Caughey, Deal, McLees, and Alben[7] have shown that the coordination of pyridine to nickel in nickel porphyrins also causes a shift of the Soret band to longer wave lengths. This effect has also been observed by Whitten, Corwin, and Baker[1] in cobalt and iron porphyrins. Loach and Calvin[8] have observed a similar shift with a manganese porphyrin and McCartin[9] with hydrated chlorophylls. The present paper records parallel observations on a variety of other porphyrin derivatives and advances an explanation of these phenomena on steric grounds similar to those proposed by Brunings and Corwin.[10]

(1) Porphyrin Studies XXVIII: paper XXVII, D. G. Whitten, E. W. Baker, and A. H. Corwin, J. Org. Chem., **28**, 2363 (1963). This work was supported in part by Research Grant A-2877 from the National Institutes of Health.

(2) National Institutes of Health Predoctoral Fellow, 1962–1963.

(3) Du Pont Fellow, 1962–1963.

(4) R. Lemberg and J. W. Legge, "Hematin Compounds and Bile Pigments," Interscience Publishers, Inc., New York, N. Y., 1949, p. 174.

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(8) P. A. Loach and M. Calvin. Biochem., **2**, 361 (1963).

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(10) K. J. Brunings and A. H. Corwin, J. Am. Chem. Soc., **64**, 593 (1942).

Transition Metal Derivatives.—In the case of nickel mesoporphyrin, the findings of Caughey, et al.,[7] were verified and extended. In the presence of very strong ligands, two Soret peaks were observed, as shown in Table I.

TABLE I

SORET SPECTRA OF NICKEL MESOPORPHYRIN IX DIMETHYL ESTER

Solution	Soret 1, mμ	Soret 2, mμ	O.D.$_1$/O.D.$_2$[b]
Pyridine, 27.5°	417	391	0.22
−11°	417	391	.60
Piperidine, 27.5°	417	393	1.24
−10°	417	393	3.31
Pyrrolidine, 27.5°	418	392	3.58
−9°	418	392	9.5
2-Methylpiperidine, 27.5°	..	392	..
DABCO[a] in benzene, 27.5°	417	393	0.67
n-Butylamine, 27.5°	415	389	.53
Ethylenimine, 27.5°	415	388	.75

[a] Diazabicyclooctane, saturated solution. The authors wish to thank the Houdry Process and Chemical Co. for this material. [b] Ratio of optical densities.

With copper complexes in weak ligand fields, only one Soret band was observed. In the presence of very strong ligands, however, two peaks were found. Cooling intensified the long wave length peak at the expense of the short where strong ligands were present. It was notably more difficult to produce the formation of two peaks for copper mesoporphyrin than for nickel mesoporphyrin. Only by cooling solutions of the copper compound in pyrrolidine or piperidine could we make the long wave length peak predominate. The results are summarized in Table II.

In contrast to the nickel and copper derivatives, zinc mesoporphyrin gives only a single Soret band. In fur-