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PROPERTIES OF SMALL RING FREE RADICALS. I. THERMAL DECOMPOSITIONS OF α-SUBSTITUTED CYCLOPROPYL PERCARBOXYLATES

R. A. Wolf* and W. Rozich

Department of Chemistry, State University College, New Paltz, New York 12561

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Several experimental techniques have evolved to differentiate between two possible mechanisms of the thermal decomposition of peroxy esters. These two mechanisms, the concerted and the non-concerted (Scheme I), have been investigated by studying activation parameters[1], the effect on rates of decomposition by changing solvent viscosity[2], deuterium isotope effects[3], volumes of activation[4], scrambling of isotopic 0-18 labeled carbonyl oxygen[5], and Hammett sigma-rho correlations[6] of many series of peroxy esters. From these studies has come solid evidence that the rates of peroxy ester decomposition (the rate of decarboxylation in the non-concerted mechanism) are highly dependent on such properties of the peroxides as conjugation, inductive polar and hybridization[7] effects. Briefly put, the more stable the R· radical the faster both decomposition mechanisms operate (the faster the rate of decarboxylation in the non-concerted mechanism, although this will have minimal effect on the overall decomposition rate if breaking the 0-0 bond is the rate determining step[8]). As the R· radical becomes more stable in a series of peroxy esters, the tendency for a shift from the non-concerted to the concerted mechanism might also be observed.

<u>Scheme I</u>

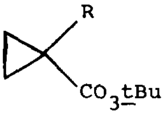
Concerted: $R\text{—}CO_3\underline{t}Bu \longrightarrow R\cdot + CO_2 + \cdot O\underline{t}Bu$

Non-Concerted: $R\text{—}CO_3\underline{t}Bu \longrightarrow R\text{—}CO_2\cdot + \cdot O\underline{t}Bu \longrightarrow R\cdot + CO_2 + \cdot O\underline{t}Bu$

We have studied the α-substituent effects of <u>t</u>-butyl cyclopropylpercarboxylates (Fig. 1). Cyclopropyl peroxyesters <u>1a</u> and <u>1c</u> have previously been studied by Rüchardt[8]. He concluded, on the basis of a careful investigation of the effects of ring size in a series of cyclic peroxyesters and 0-18 labeling experiments, that the α-H- and α-CH_3- substituted cyclic peroxyesters decompose by a non-concerted mechanism.

His conclusions as to the non-concerted nature of the decomposition of <u>1a</u>

Fig. 1



1a, R=H
1b, R=D
1c, $R=CH_3$
1d, R=aryl

and 1c seem to be born out by the results of our investigations of a larger series of α-substituted t-butyl cyclopropylpercarboxylates. The first-order rate constants, averaged over three or more runs, and the relative standard deviations for the average rate constants for the thermal decomposition of 1a-1d are given in Table I. Each individual kinetic run was determined over at least two half-lives. In all individual runs no deviation from the straight line was observed. The standard errors for the individual runs were less than the relative standard deviations for the average of each set. Each run gave a straight line with a correlation coefficient of greater than 0.998. The rates were determined by following the rate of disappearance of the carbonyl stretching peak by ir. The rate constant for 1a is similar to the value for the decomposition of the same compound in ethyl benzene, as determined by Rüchardt[8].

The rate of decomposition of t-butyl cyclopropyl percarboxylate (R=H) represents an 11-fold decrease from the decomposition rate of the acyclic isopropyl peroxy ester analog. This fact, together with the absence of an α-deuterium isotope effect, the relatively small rate enhancement when methyl or phenyl groups are put in the 1-position, the decrease in rate upon changing from 2,2, 4-trimethylpentane to more viscous solvent of similar polarity (dodecane) and the relatively high enthalpies and entropies of activation (Table I) suggest that these peroxy esters decompose by a non-concerted, two-step mechanism.

A Hammett plot of the rates of decomposition of para-aryl-substituted 1d gives a reasonable correlation only with $\sigma+$ ($\rho = -0.31 \pm 0.06$, correlation coefficient = 0.94_6) and not at all with σ or σ_I. The p-NO_2 point lies considerably above the σ^+ plot (i.e., p-$NO_2C_6H_4$ decomposes faster than predicted). Omission of the p-NO_2 point improves the overall plot vs. σ^+ considerably ($\rho = -0.47 \pm 0.02$, correlation coefficient = 0.99_3). Two features of this Hammett plot stand out. The first is the correlation with sigmas of strong resonance effect character (σ^+). This seems at odds with the small rho values and the other experimental data which support the non-concerted nature of the decomposition mechanism. The second is the divergence of the p-NO_2 point from the otherwise excellent correlation of the para-substituent groups.

These apparent anomalies might be resolved by suggesting a mixed mechanism (part concerted and part non-concerted) for the t-butyl cyclopropyl percarboxylates. In going from 1a and 1d (p-NO_2) to 1c and the more electron-donating para groups of 1d, the mechanism may be shifting to a higher percentage of concerted decomposition. If this is true, much of the data in Table I would be of questionable value as far as being used per se to differentiate between the two

Table I

First-Order Rate Constants ($\times 10^4$, in sec^{-1} at 113.0°C.), Activation Parameters and Solvent Viscosity Effects on Some Substituted t-butyl Cyclopropyl Percarboxylates.

R	Rate Constant[a]	ΔH^{*b}	ΔS^{*c}	k(C-8)/k(c-12)[d]	k(predicted)[f]
H	0.678 ± 0.008	36.0	15.1	1.13 ± 0.02	
D	0.678 ± 0.006	----	----	-----------	
CH_3	0.956 ± 0.011	32.9	7.9	-----------	
C_6H_5	0.896 ± 0.006	33.2	8.5	1.03 ± 0.01	1.13
p-$CH_3OC_6H_4$	2.13 ± 0.02	31.8	6.6	-----------	1.35
p-$CH_3C_6H_4$	1.19 ± 0.01	32.9	8.1	1.03 ± 0.02	1.26
p-ClC_6H_4	0.861 ± 0.001	32.5	6.5	1.05 ± 0.01	0.97
p-$NO_2C_6H_4$	0.670 ± 0.022	34.4	11.0	0.95 ± 0.04[e]	(0.67)

a) Average of at least three kinetic runs, 2,2,4-trimethylpentane solvent.

b) The maximum standard errors for ΔH^* are ± 1.6 kcal/mole.

c) The maximum standard errors for ΔS^* are ± 4.2 eu.

d) Rate constant for 2,2,4-trimethylpentane over that for n-dodecane.

e) k(C-8)/k(hexadecane) = 1.07 ± 0.04, for p-$NO_2C_6H_4$.

f) Predicted "non-concerted" rate constant. ($\times 10^4$, in sec^{-1} at 113.0°C).

mechanisms. Thus the activation parameters would be of little meaning, since they might be a composite of contributions from the two mechanisms. The relatively insensitive solvent viscosity effects might also be of limited usefulness since these effects would be felt mainly by that part of the mixed mechanism that is most sensitive to changes in solvent viscosity (namely, non-concerted).

The para-nitro substituted peroxy ester in the t-butyl phenylperacetate series is believed to have some partial non-concerted character in its thermal decomposition[2,9]. If one assumes that the 1d (p-NO_2) peroxyester is decomposing entirely by the non-concerted mechanism (an arbitrary assumption given the present data, but note the similar rate constants for 1a and 1d (p-NO_2)), one could estimate the amounts of concerted character in the other 1d peroxyesters. Assuming an attenuation factor on the rho of 0.43[10] due to the interposition of a saturated carbon between the benzene ring and the carboxyl group and using the rho value (-0.676 vs σ) for the t-butyl perbenzoates[6], one estimates a "non-concerted" rho (ρ') of -0.29 for the 1d peroxy esters for those parts of the reaction that decompose via non-concerted mechanism:

$$\rho' = \rho(\text{perbenzoates}) \times 0.43$$
$$\log k\ (\text{predicted}) = \rho'\ (\ \sigma(x)\ - \sigma(NO_2)) + \log k\ (NO_2)$$

Using this estimated "non-concerted" rho, one can calculate the predicted non-concerted rates for other substituent groups. These predicted rates are compared with the actual experimental rates in Table I.

Of course, the predicted rate constants should all be less than or equal to the actual rate constants. Any "excess" rate of actual rates as compared to predicted rates would then be attributed to the concerted mechanism. The fact that the predicted rates are *larger* than experimental (except for *p*-CH_3O) indicates the possible arbitrariness of the damping factor we used to calculate our estimated "non-concerted" rho. One would hope that an attenuation factor which more accurately measured the transmission of polar effects through a cyclopropane carbon (i.e., through two exo bonds of enhanced S character) would show a steady and increasing divergence between predicted and actual rate constants in going to *para* groups of greater electron-donating power.

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