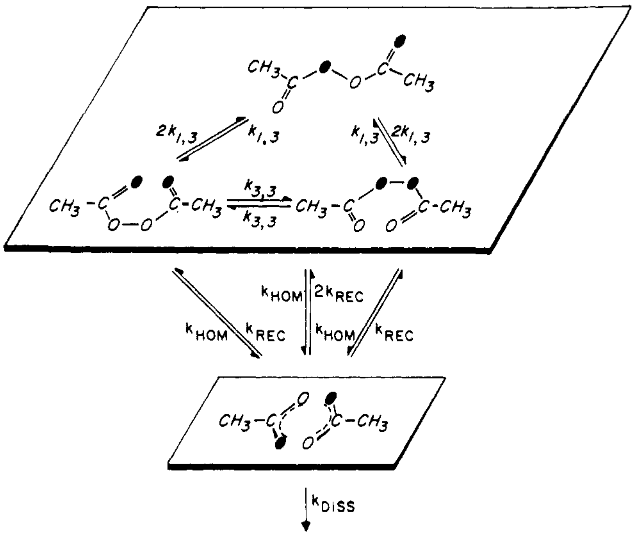

$$\lambda_D = k_{HOM}(1-f_R) \qquad f_R = 4k_{REC}/(4k_{REC}+k_{DISS})$$

$$\lambda_{TS} = k_{HOM}f_R + 2(k_{3,3}+k_{1,3})$$

$$\lambda_{RS} = k_{HOM}f_R + 4k_{1,3}$$

Figure 2. Oxygen scrambling in acetyl peroxide.

ination by any one path can be detected (homolysis, $\lambda_{RS} = \lambda_{TS}$; [1,3]sigmatropy, $\lambda_{RS} = 2\lambda_{TS}$; [3,3]-sigmatropy, $\lambda_{RS} = 0$). The relative contributions of two (but not all three) can be evaluated.[14]

Table I. Oxygen Scrambling of Acetyl Peroxide[a]

Solvent	Temp, °C	n[b]	$10^6\lambda_{TS}$	$10^6\lambda_{RS}$	$10^6\lambda_D$	f_R[c]
Cumene	44.4	4	0.21 ±0.03	0.10 ±0.05	0.49[d] ±0.02	0.19 ±0.10
	55.1	13	1.29 ±0.05	0.75 ±0.08	1.78 ±0.04	0.30 ±0.04
Isooctane	44.4	5	0.37 ±0.04	0.11 ±0.05	0.64[e] ±0.06	0.15 ±0.07
	55.1	12	1.61 ±0.13	1.18 ±0.21	2.75 ±0.05	0.30 ±0.06

[a] Uncertainties are standard deviations.[10] [b] Number of independent samples subjected to ^{18}O analysis. [c] Fractional extent of acetoxy return if $k_{1,3} = 0$. [d] Obtained by M. Yoshida. [e] Obtained titrimetrically by J. D. Lassila. All other λ_D's were obtained manometrically.

That [3,3]shifts are important in this system is thus required by the observation that $(\lambda_{TS} - \lambda_{RS})$ [$= 2(k_{3,3} - k_{1,3})$] > 0 in all investigated environments. That these cannot constitute the sole path for oxygen scrambling is required by the observation that $\lambda_{RS} > 0$. Less certain, thus far, are the relative contributions of [1,3]shift and acetoxy recombination to the remaining ("random") scrambling. Considering the matter further elsewhere,[15] we now merely note the consequences of the two extreme hypotheses. (a) Should acetoxy radical pairs be absent or (equivalently) produced irreversibly ($f_R = 0$), [3,3]sigmatropy would account for 63–85% of oxygen scrambling. Alternatively (b), should [1,3]shifts be entirely absent, the [3,3] mechanism would contribute 25–54% of the scrambling. This latter possibility would then require $f_R = \lambda_{RS}/(\lambda_D + \lambda_{RS})$. Such values of f_R (Table I) are more generally to be regarded as *upper limits* to the fraction of acetoxy pairs that may recombine. In either case, as expected, [3,3]sigmatropy contributes less at the higher temperature.

Finally, we note the gratifying agreement between our isooctane ratios of $\lambda_{TS}/(\lambda_{TS} + \lambda_D)$, 0.37 at either 44.4 or 55.1°, and that reported by Martin, *et al.*, 0.38 at 80°.[6b,c] Their premature identification of this ratio as f_R followed (in part) from their belief that "no more than 1% of the reaction can proceed by mechanism A" (the [3,3]sigmatropic shift). Whether their failure to detect this mechanism is best ascribed to (a) their higher reaction temperature (80°), (b) their lower ^{18}O enrichment (3.6%), or (c) the fewer samples they felt obliged to analyze (1) is as yet unclear. Much more puzzling is the failure of Szwarc, *et al.*,[6a] to detect *any* scrambling under conditions where the concordant data would have predicted 38%.

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[13] (a) W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962); (b) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **89**, 1741 (967); (c) T. Koenig, *ibid.*, **91**, 2558 (1969); (d) W. G. Bentrude, *Ann. Rev. Phys. Chem.*, **18**, 283 (1967).

[14] Aliphatic displacement stereochemistry is precisely analogous; the relative contributions of distinct inversion, retention, and racemization mechanisms can never all be completely determined.

[15] M. J. Goldstein and H. A. Judson, *J. Amer. Chem. Soc.*, **92**, 4120 (1970).

[1,3]Sigmatropic Shifts in Peroxidic Compounds

Sir:

The mechanistic ambiguities of oxygen scrambling in peroxidic compounds[1] could not be appreciated, much less disentangled, until the early consistent failures even to detect the reaction were rectified. With two such claims[2a,b] now disposed of,[1,3] we here remove the third and last[2c] by reporting oxygen scrambling of *t*-butyl perbenzoate. Extending this pattern also to include *t*-butyl peracetate[4] and perpivalate, we now find quantitative disagreement with expectations to be derived from current mechanistic thinking.

Each of the three carbonyl ^{18}O-enriched peresters was prepared from the sodium salt of *t*-butyl hydroperoxide and the appropriate acid chloride which derived, in turn, from the nitrile and "1.5%" enriched $H_2{}^{18}O$. Concordant assays of >98% were obtained by nmr, by CO_2 evolution (peracetate and perpivalate), and by titration[5] (peracetate and perbenzoate). Deg-

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[1] M. J. Goldstein and H. A. Judson, *J. Amer. Chem. Soc.*, **92**, 4119 (1970).

[2] (a) Acetyl peroxide, L. Herk, M. Feld, and M. Szwarc, *ibid.*, **83**, 2998 (1961); (b) benzoyl peroxide, M. Kobayashi, H. Minato, and Y. Ogi, *Bull. Chem. Soc. Jap.*, **41**, 2822 (1968); (c) *t*-butyl perbenzoate, J. C. Martin and T. W. Koeing, *J. Amer. Chem. Soc.*, **86**, 1771 (1964), footnote 21.

[3] (a) Acetyl peroxide, J. W. Taylor and J. C. Martin, *ibid.*, **89**, 6904 (1967); (b) benzoyl peroxide, J. C. Martin and J. H. Hargis, *ibid.*, **91**, 5399 (1969).

[4] T. Koeing and M. Deinzer, *ibid.*, **90**, 7014 (1968), have independently discovered oxygen scrambling accompanying peracetate decomposition in paraffin oil solution.

radation of the peroxidic oxygens to the molecular species and isotopic analysis of the latter was achieved essentially as reported elsewhere for acetyl peroxide[1] except that only a 34/32 *m/e* ratio (*R*) was here obtained. Similar control experiments, applied however only to the most vulnerable perpivalate, yielded correspondingly reassuring results.

With the [3,3]sigmatropic shift now structurally precluded, Figure 1 reveals the accessibility of only a single experimental scrambling rate constant (λ_S). Extracted by nonlinear least-squares fitting of *R* to eq 1 and 2,[6] λ_S differs only by a statistical factor from the

$$R = N_1/(1 - N_1) \qquad (1)$$

$$N_1 = c[(1 - 2p)/2] + p[(3 - 2p)/2] - (c - p)[(1 - 2p)/2]e^{-\lambda_S t} \qquad (2)$$

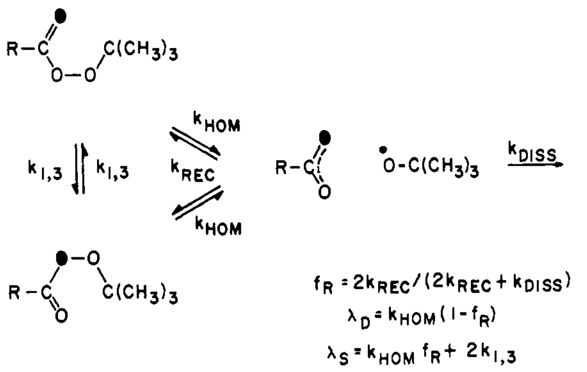
mechanistically identical λ_{RS}, the rate constant for "random scrambling" of acetyl peroxide that remains after the contribution of [3,3]sigmatropy is removed. Such data are collected in Table I together with f_R (the *maximum* fraction of radical pair return, should $k_{1,3} = 0$).

Table I. Random Scrambling, Cumene Solution[a]

	Temp, °C	n^b	$10^6\lambda_S$	$10^6\lambda_D{}^c$	$f_R{}^d$
t-Butyl perbenzoate	105.5	9	4.2 ±0.2	17.5 ±0.2	0.19 ±0.01
t-Butyl peracetate	105.5	8	17.0 ±0.8	23.7 ±0.4	0.42 ±0.02
t-Butyl perpivalate	50.5	6	0.25 ±0.11	9.6 ±0.2	0.025 ±0.011
Acetyl peroxide	55.1	13	0.75[e] ±0.08	1.78 ±0.04	0.30 ±0.04
	44.4	4	0.10[e] ±0.05	0.49 ±0.02	0.19 ±0.10

[a] Uncertainties are standard deviations. [b] Number of independent samples subjected to ^{18}O analysis. [c] Obtained manometrically by M. Yoshida. [d] Fractional extent of return if $k_{1,3} = 0$. [e] λ_{RS} from ref 1.

Heretofore, such phenomena have uniformly been interpreted as resulting from radical pair recombination within a solvent cage and their viscosity dependence has been subjected to particular scrutiny[3,4,7,8] Apart from serious questions of quantitative reliability,[9,10d,e] it is qualitatively obvious that such an approach must remain mechanistically indecisive until the viscosity dependence of the alternative [1,3]sigmatropic mechanism is revealed. We note that the continued neglect of this alternative now raises three new problems.



$$f_R = 2k_{REC}/(2k_{REC} + k_{DISS})$$

$$\lambda_D = k_{HOM}(1 - f_R)$$

$$\lambda_S = k_{HOM}f_R + 2k_{1,3}$$

Figure 1. Competing mechanisms for oxygen scrambling in peresters.

(a) Hitherto, *t*-butyl perpivalate was believed to decompose by a concerted mechanism[11] that entirely avoids the unstable pivaloyloxy radical. The observed oxygen scrambling would now, however minimally, appear to require its reintroduction.

(b) The lower f_R for the perbenzoate than for the peracetate recalls both a similar claim for the corresponding diacyl peroxides[3b] and its appropriate description, "surprising." Given that the acetoxy radical surely decarboxylates (and probably diffuses) more rapidly than the benzoyloxy, one must now invent a new barrier to the recombination of this second radical with its cage partner or else render its oxygens nonequivalent.[12]

(c) The unprecedented increase in acetyl peroxide f_R with increasing temperature[10] would require that $(\Delta H_{Rec} - \Delta H_{Diss})$ be 17 and 11 kcal/mol in isooctane and in cumene solutions. With ΔH_{Diss} including both those of decarboxylation (*ca.* 5–7 kcal/mol)[2a,10a] and diffusion (*ca.* 2–3 kcal/mol),[13] we find the resulting estimates of ΔH_{Rec} (however crudely attained) to be totally incredible.

In summary, the consistent interpretation of oxygen scrambling as a radical cage phenomenon would seem to demand an added *post hoc* hypothesis each time it appears.[14] With the [3,3]sigmatropic shift now firmly established as a contributor to acetyl peroxide scrambling,[1] we think it altogether simpler to believe that the corresponding [1,3] mechanism must play *some* role in the oxygen scrambling of these peroxidic compounds. Obviously inadequate to define this role in any quantitative manner, the current data should nevertheless still serve the important (if negative) function of discouraging the routine use of oxygen scrambling as a test for, or measure of, acyloxy radical recombination.

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(5) L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).

(6) N_1 is the *mole* fraction of $O_2{}^{34}$; *c* and *p* are the initial *atom* fractions O^{18} in one carbonyl and in one peroxidic position. As before,[1] experimentally determined rate constants are denoted by λ, mechanistically defined ones by *k*.

(7) T. Koeing, *J. Amer. Chem. Soc.*, **91**, 2558 (1959).

(8) J. C. Martin and S. A. Dombchik, *Advan. Chem. Ser.*, **No. 75**, 209 (1968).

(9) H. Kiefer and T. G. Traylor, *J. Amer. Chem. Soc.*, **89**, 6667 (1967); S. A. Wiener and G. S. Hammond, *ibid.*, **91**, 986 (1969).

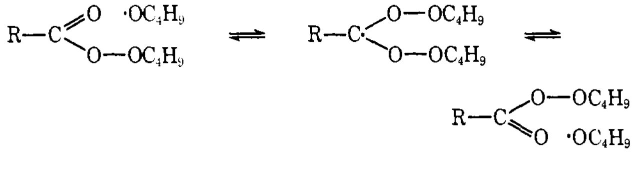
(10) (a) W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962); (b) S. Kodama, *Bull. Chem. Soc. Jap.*, **35**, 652, 658, 824, 827 (1962); (c) S. F. Nelsen and P. D. Bartlett, *J. Amer. Chem. Soc.*, 88, 143 (1966); (d) O. Dobis, J. M. Pearson, and M. Szwarc, *ibid.*, **90**, 278 (1968); (e) K. Chakravorty, J. M. Pearson, and M. Szwarc, *ibid.*, **90**, 283 (1968).

(11) P. D. Bartlett and D. M. Simons, *ibid.*, **82**, 1753 (1960); T. Koeing and R. Wolf, *ibid.*, **89**, 2948 (1967).

(12) *Cf.* W. G. Bentrude and J. C. Martin, *ibid.*, **84**, 1561 (1962), structure XV.

(13) $\Delta H_{Diss} = \Sigma f_i \Delta H_i$ where ΔH_i and f_i are the activation enthalpies and fractions of the total k_{Diss} that are contributed by each such irreversible path.

(14) Yet another has been suggested by a referee.



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Acetyl Peroxide Heavy Atom Kinetic Isotope Effects. A Reevaluation

Sir:

Although the "exact analysis"[1] of heavy atom kinetic isotope effects promises to provide a new and potentially powerful tool for the elucidation of transition state structure,[2] its scope and limitations remain still obscure. Only recently begun,[3] the task of extensive testing and application has naturally tended to rely upon older methods of gas purification, mass spectrometry, and data analysis to generate the experimental kinetic isotope effects needed.

We were therefore troubled to find that the very first report[3a,4] of such an exact analysis has since been criticized on experimental rather than on theoretical grounds.[5] Spurious results, it was claimed, are often encountered in the traditional method of determining such isotope effects: the comparison of isotope ratios obtained from initially formed product (R_f) with those of complete reaction (R_l, eq 1).[6,7] The

$$k_l/k_h = \ln\left[1 - f\left(\frac{1+R_l}{1+R_f}\right)\left(\frac{1-R_f}{1-R_l}\right)\right] \Bigg/ \ln\left[1 - f\left(\frac{R_f}{R_l}\right)\left(\frac{1+R_l}{1+R_f}\right)\right] \quad (1)$$

obvious culprit, contamination of the initially formed product samples, was still more strongly implicated by the subsequent independent claim[8] that our published carbon dioxide purification techniques[3b] were inadequate for their intended use. To eliminate such errors, the analysis of successive product fractions was instead recommended. This did indeed provide a carbon isotope effect of "less than 1.016"[5] in contrast with our previously published 1.023 ± 0.003.[3a]

Concerned by the consequences of such criticism, we have now repeated the original determinations, extended the initial product range from 6 to 17%, chosen a second reaction solvent (from which the acetyl peroxide was also subjected to its final recrystallization), and used some of the "10%" carbonyl ^{18}O-enriched substrate originally prepared for another purpose.[9] These, we would think, should provide ample opportunity to observe the consequences of otherwise hidden impurities. The results shown in Table I leave little question as to the reproducibility and reliability (if not also the accuracy) of the originally published data. Of particular note is the insensitivity of our oxygen isotope effects to a 50-fold variation in ^{18}O distribution between carbonyl and peroxidic oxygens, a necessary consequence of oxygen scrambling.[9,10]

Table I. Carboxyl Kinetic Isotope Effects[a]

Solvent	Temp, °C	$f_{\max}$[b]	n[c]	k_{12}/k_{13}	k_{16}/k_{18}
Cumene	44.7	0.05	9	1.019 ±0.001	1.035 ±0.002
	44.7	0.15	5	1.016[d] ±0.007	1.0337[d] ±0.0007
Isooctane	44.8	0.06	5	1.023[g] ±0.003	1.023[g] ±0.007
	44.4	0.13	3	1.0212 ±0.0001	1.027 ±0.001
	44.7	0.17	6	1.023[d] ±0.002	1.029[d] ±0.002
	80			*<1.016*[i]	*1.033*[i]
	74	0.07	6		*1.021*[e,h]
	74	0.07	6		*1.020*[f,h]

[a] Uncertainties are standard deviations; isotopic abundances are at natural levels except where noted otherwise; italicized entries are from other laboratories. [b] Maximum extent of partial decomposition. [c] Number of independent partially decomposed samples analyzed. [d] 10% carbonyl ^{18}O-enriched. [e] Hexadeuterated. [f] 1.4% carbonyl ^{18}O-enriched. [g] Reference 3a. [h] Reference 8. [i] Reference 5.

We chose not to employ the recommended[5] method of successive product fractions[11] because: (a) the expected[5] linear plot of "ln *A*" *vs.* ln (1 − *f*) should in fact obtain only in the limit of infinitely small product fractions, an experimentally inconvenient restriction. (b) Finite fractions require the use of equations, properly judged to be "awkward. . .for systematic treatment of the experimental data."[7] (c) All such equations presume an infinitely small isotope ratio. Well-justified in the ^{14}C studies for which they were originally intended,[11] their application to our own heavy isotope abundances of 0.4–10% seemed questionable.[12]

Curiously, the same authors[5] also reported determination of a methyl carbon isotope effect, k_{12}/k_{13} = "1.005–1.010," that appeared to provide unanticipated support for our original mechanistic conclusion.[3a] Repeating their approach (CuO oxidation of the methane product), but using traditional methods of purification and analysis, we now find their published data to be consistent only in their unreliability. In two solvents, the carbon isotope effect at the methyl is less than

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(1) M. Wolfsberg, *Ann. Rev. Phys. Chem.*, **20**, 449 (1969); M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 225, 325 (1964); *J. Chem. Phys.*, **45**, 2618, 4105 (1966).

(2) M. J. Goldstein, *Science*, **154**, 1616 (1966).

(3) (a) M. J. Goldstein, *Tetrahedron Lett.*, 1601 (1964); (b) M. J. Goldstein and G. L. Thayer, Jr., *J. Amer. Chem. Soc.*, **87**, 1933 (1965); (c) S. Seltzer and S. M. Mylonakis, *ibid.*, **89**, 6584 (1967); (d) S. Seltzer, A. Tsolis, and D. B. Denney, *ibid.*, **91**, 4236 (1969); (e) A. M. Katz and W. H. Saunders, Jr., *ibid.*, **91**, 4469 (1969).

(4) An earlier application to deuterium isotope effects was reported by A. V. Willi, *Helv. Chim. Acta*, **47**, 647, 655, 837 (1964).

(5) J. W. Taylor and J. C. Martin, *J. Amer. Chem. Soc.*, **89**, 6904 (1967).

(6) This differs from eq V.21 of ref 7 only by its inclusion of the numerically insignificant $(1 - R_f)/(1 - R_l)$ term that arises whenever 2 mol of analyzed product (CO_2) is formed. *Cf.* J. Warkentin and D. M. Singleton, *Can. J. Chem.*, **45**, 3045 (1967).

(7) J. Bigeleisen and M. Wolfsberg, *Advan. Chem. Phys.*, **1**, 15 (1958).

(8) T. Koenig and R. Cruthoff, *J. Amer. Chem. Soc.*, **91**, 2562 (1969).

(9) M. J. Goldstein and H. A. Judson, *ibid.*, **92**, 4119 (1970).

(10) More rigorously, such insensitivity should always follow so long as the difference between rates of scrambling and decomposition exceeds the difference between the decomposition rates of isotopically differing reactants. For the dependence of apparent isotope effect on isotopic distribution in the absence of scrambling, see eq A2 in ref 3b.

(11) A. M. Downes, *Aust. J. Chem. Res.*, **5**, 521 (1952).

(12) The results of ref 5 derive from 5% ^{13}C-enriched substrate. No details of fraction size were provided.