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Competitive Dissociation and Rearrangements of Acetyl Peroxide¹

Sir:

Hardly a corner of organic chemistry remains untouched by the idea of incomplete dissociative return.² In the case of acetyl peroxide^{3a} (or, more generally, of any acyclic precursor of free radicals^{3b,c}) it appears clothed as the solvent cage model.⁴ Thermal isomerizations of cyclic hydrocarbons similarly have their biradicals, anionic rearrangements and solvolytic transformations their ion pairs.

Only rarely has it explicitly been recognized that such observations are often equally well understood to result from concerted reaction mechanisms.^{5,6} Only once to our knowledge, in the particular case of azomethane photolysis, has such an alternative unambiguously been excluded.⁷

We here report a similarly designed experiment which, no less unambiguously, requires precisely the opposite conclusion. The ¹⁸O scrambling of acetyl peroxide (Figure 1) is now most simply understood to result exclusively from competing [1,3]- and [3,3]sigmatropic shifts both in solution and in the gas phase. The alternative hypothesis—geminate recombination within a solvent cage—was previously shown to be neither necessary nor sufficient to account for ¹⁸O scrambling in solution.^{6a} We now demonstrate that this hypothesis also grossly misjudges the possibility of ¹⁸O scrambling in the gas phase.

The earlier investigation had successfully isolated the contribution of [3,3]sigmatropy, both in cumene and in isooctane solution. But it could not distinguish the two possible supplementary contributors (solvent cage recombination and/or [1,3]sigmatropy). This failure is now recognizable within a more general context.

Applying the linear analysis of labeling experiments,⁸ any mechanistic subgraph like Figure 1 requires

$$\chi_t = \chi_t(0)e^{-\lambda t} \quad (1)$$

Its twofold symmetry defines the eigenfunctions

$$\begin{aligned} \chi_1 &= [A_1] + [A_2] + [A_3] \\ \chi_2 &= [A_1] - [A_2] + [A_3] \\ \chi_3 &= [A_1] \quad \quad \quad - [A_3] \end{aligned} \quad (2)$$

Although the product vertex ($2\text{CH}_3 \cdot + 2\text{CO}_2^{46}$) is omitted,⁹ the corresponding eigenvalues (eq 3) must still include the formation of product—either by the dissociation of solvent-caged radical pair (k_{DIS}) and/or by the irreversible trans-

formation of acetyl peroxide to product (k_{PRO}); f_R is the fraction of return from radical pairs ($f_R \equiv 4k_{\text{REC}}/(4k_{\text{REC}} + k_{\text{DIS}})$).¹⁰

$$\lambda_1 = k_{\text{PRO}} + k_{\text{HOM}}(1 - f_R)$$

$$\lambda_2 = k_{\text{PRO}} + k_{\text{HOM}} + 4k_{1,3} \quad (3)$$

$$\lambda_3 = k_{\text{PRO}} + k_{\text{HOM}} + 2k_{1,3} + 2k_{3,3}$$

The previous discovery—that λ_3 uniformly exceeds λ_2 —could therefore only require that $k_{3,3}$ exceed $k_{1,3}$. Neither the absolute nor the relative values of five mechanistic parameters can ever be defined by three experimental ones ($\lambda_i, i = 1, 3$).

The present investigation simplifies matters by contending that any semantically unambiguous model of a solvent cage⁴ must include a solvent.¹¹ In the gas phase, k_{HOM} must vanish. Three experimental rate constants can then provide three mechanistic ones.

As before,^{6a} the two isotope ratios ($R_1 = I_{34}/I_{32}$, $R_2 = I_{36}/I_{34}$) of molecular oxygen (derived exclusively from the peroxidic positions) were used to obtain two of the three experimental rate constants—"total scrambling" ($\lambda_{\text{TS}} \equiv \lambda_3 - \lambda_1$) and "random scrambling" ($\lambda_{\text{RS}} \equiv \lambda_2 - \lambda_1$). The third ("decomposition," λ_1) was concurrently obtained by gas chromatography. With acetyl peroxide at ~ 7 Torr and isopentane at ~ 600 Torr, the CO_2 yield was $99 \pm 1\%$.¹² Rate constants were insensitive to either a 15-fold increase in glass surface area or to tenfold dilution.

Perhaps the most decisive results of Table I are the dis-

Table I. Experimental Rate Constants^a

		Cumene ^b	Isooctane ^b	Gas
$10^3\lambda_1$ Decom- position	44.1°	0.49 ± 0.02	0.64 ± 0.06	0.45 ± 0.01
	55.0°	1.79 ± 0.04	2.75 ± 0.05	2.29 ± 0.06
	65.5°			9.48 ± 0.64
	75.5°			41.0 ± 5.6
$10^3(\lambda_2 - \lambda_1)$ Random scrambling	44.1°	0.10 ± 0.05	0.11 ± 0.05	0.27 ± 0.01
	55.0°	0.75 ± 0.08	1.18 ± 0.21	1.58 ± 0.14
	65.5°			5.54 ± 0.15
	75.5°			20.20 ± 0.41
$10^3(\lambda_3 - \lambda_1)$ Total scrambling	44.1°	0.21 ± 0.03	0.37 ± 0.04	0.38 ± 0.02
	55.0°	1.29 ± 0.05	1.61 ± 0.13	1.67 ± 0.17
	65.5°			7.93 ± 0.41
	75.5°			28.4 ± 1.0

^a Each rate constant derives from nonlinear least-squares fitting of 4–13 experimental points; uncertainties are standard deviations; ¹⁸O-enrichment: 10% for the 55° run, 45% for the others.
^b Reference 6a.

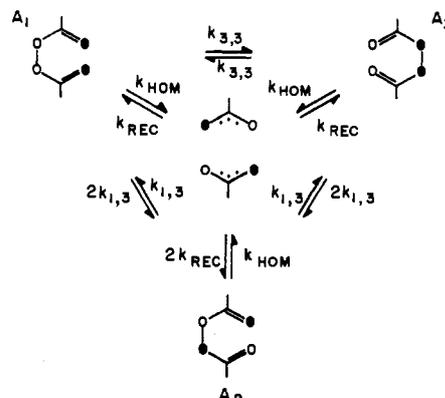


Figure 1. Three mechanisms for the ¹⁸O scrambling of acetyl peroxide. Others are possible.¹⁰

Table II. Gas Phase Mechanistic Rate Constants and Activation Parameters

Temperature	$10^7 k_{\text{PRO}}$	$10^7 k_{3,3}$	$10^7 k_{1,3}$
44.1°	4.5 ± 0.1	1.2 ± 0.1	0.68 ± 0.03
55.0°	22.9 ± 0.6	4.4 ± 0.9	4.0 ± 0.3
65.5°	95 ± 6	26 ± 2	13.9 ± 0.4
75.5°	410 ± 56	92 ± 5	51 ± 1
E_a^a	30.7 ± 0.9 ^b	30.4 ± 0.5	30.0 ± 0.2
$10^{14} A$	6.5 ± 8.0 ^b	1.0 ± 0.8	0.3 ± 0.1
ΔH^*	30.0 ± 0.8	29.7 ± 0.5	29.4 ± 0.2
ΔS^*	7.0 ± 2.5	3.3 ± 1.5	1.2 ± 0.7

^a Each pair of activation parameters derives from concurrent nonlinear least squares fitting of experimental observables at all temperatures; uncertainties are standard deviations. ^b Literature parameters^{12a} ($E_a = 29.5$, $10^{14} A = 1.8$) consistently extrapolate to k_{PRO} values 30–50% higher than those observed.

crepancies between λ_2 and λ_1 . From eq 3, these should vanish in the gas phase if [1,3]sigmatropy were entirely absent in solution. Not only do they fail to vanish but their magnitudes are hardly changed. Neither are any of the three experimental rate constants appreciably different from their values in solution. The results agree entirely with expectation for competing multicenter transformations. The solvent is experimentally irrelevant.

Transformation into mechanistic rate constants (Table II) reveals that $k_{\text{PRO}} > k_{3,3} > k_{1,3}$ throughout, but with hardly any detectable effect on the activation parameters. Of more general importance, here as well as in the higher temperature Cope rearrangement of 1,5-hexadiene,¹³ an acyclic [3,3]sigmatropic shift is no longer associated with the abnormally negative ΔS^* ¹⁴ hitherto believed to be its hallmark.¹⁶ It thus follows that such abnormal values ought no longer be ascribed to the simple loss of internal rotation that accompanies the transformation of an acyclic reactant to a cyclic transition state.¹⁷ A similar lesson is provided by the recently reported converse observation of an abnormally negative ΔS^* in the cyclic [3,3]sigmatropic shift of 1,4-dimethylenecyclohexane.¹⁸ The increasingly popular 1,4-cyclohexanediyl intermediate^{15,18,19} may well provide a new and conveniently consistent way to rationalize the appearance of such abnormal values.

These results also suggest a different perspective on the apparently variable stereoselectivity of numerous heterosigmatropic rearrangements. As each CH_2 of 1,5-hexadiene is replaced, first by NH and then by O, the isoconjugate series finds its practical terminus at acetyl peroxide. As it does, the energy gaps which separate competing mechanisms¹³ are greatly compressed. [3,3]Sigmatropy retains its advantage over [1,3]sigmatropy but dissociation overtakes them both.²⁰

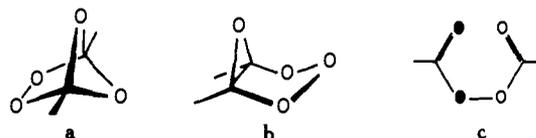
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Supplementary Material Available. Algebraic as well as experimental details, representative plots, and a complete tabular survey of all experimental data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order

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(b) Algebraic as well as experimental details, representative plots, and a complete tabular survey of all the experimental data will appear following these pages in the microfilm edition of this volume of the journal. See paragraph at end of paper regarding supplementary material.

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