# Thermochemistry and Estimated Activation Parameters for the Thermal Decomposition of 1,2-Dioxetanedione, 4-tert-Butyl-1,2-dioxetan-3-one, and 4,4-Dimethyl-1,2-dioxetan-3-one

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Abstract: Thermochemical values and activation parameters are estimated for the thermal decomposition of 1,2-dioxetanedione (1), 4-tert-butyl-1,2-dioxetan-3-one (2a), and 4,4-dimethyl-1,2-dioxetan-3-one (2b). These cyclic peroxides are important to chemiluminescent processes and there is an interest in their isolation. Our intent is to provide an estimate of activation parameters which would be useful in choosing conditions under which they may be isolated, and to check an approximate half-life reported for one of these cyclic peroxides (2a). The calculated activation parameters for the 1,2-dioxetanes are: 1, E = 16.7 kcal/mol, log A = 12.6; 2a, E = 22.0 kcal/mol, log A = 12.6; and 2b, E = 20.9 kcal/mol, log A = 12.8. At 27°, this corresponds to lifetimes of 0.34, 2500, and 250 sec for 1, 2a, and 2b, respectively. The observed and calculated half-lives for 2a are in good agreement. With regard to the chemiluminescent reactions of 1, it is concluded from the calculated thermochemical data that sufficient energy is released from the decomposition of 1 to produce a triplet carbon dioxide molecule, but not the lowest energy excited state singlet species.

Various derivatives of oxalic acid undergo reaction with hydrogen peroxide to produce light in the presence of appropriate acceptors.[1] In fact, one such system is apparently the basis for a commercial chemical light device.[1k,2] It is proposed that chemiluminescence may result from the reaction sequence (eq 1 and 2) where 1,2-dioxetanedione (1) is formed from the

$$\text{(structure)} \xrightarrow{A} 2CO_2 + A^* \qquad (1)$$

$$A^* \longrightarrow A + h\nu \qquad (2)$$
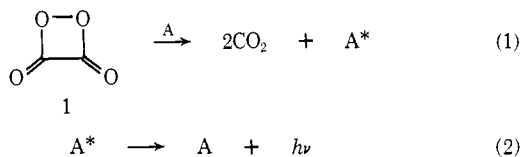
oxalate derivative and hydrogen peroxide, and A is the acceptor.[1a] Similarly, energy obtained from the decomposition of 1 may be transferred to a molecule that subsequently undergoes reaction from an excited state.[1j] Although alkyl,[3] arylalkyl,[3c] and alkoxy[4]

substituted 1,2-dioxetanes have been isolated, the isolation of 1 has not been reported.[5] The related 1,2-dioxetan-3-one system (2) is of particular interest, since

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such an intermediate is proposed in the bioluminescence of the North American firefly (*Photinus pyralis*).[8] The cyclic peroxide 3 is suggested to result from lucerifin,

3
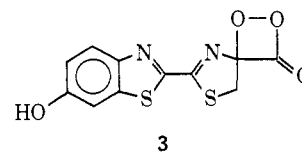
ATP, oxygen, and luciferase in the presence of magnesium ions. Recently, 4-tert-butyl-1,2-dioxetan-3-one (2a, R_1 = t-C$_4$H$_9$; R_2 = H) has been isolated.[9] This is the first reported isolation of a 1,2-dioxetan-3-one, although these cyclic peroxides have been proposed as intermediates in the reaction of singlet oxygen with ketenes.[10]

Considering the interest in these two cyclic peroxide systems (1 and 2), we have calculated thermochemical and kinetic activation parameters for 1, 2a (R_1 = t-C$_4$H$_9$, R_2 = H), and 2b (R_1 = R_2 = CH$_3$). The success of our previous calculations of kinetic activation parameters for 1,2-dioxetanes,[3c,11] based on a two-step
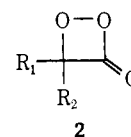
(1) (a) M. M. Rauhut, *Accounts Chem. Res.*, 2, 80 (1969); (b) E. A. Chandross, *Tetrahedron Lett.*, 761 (1963); (c) M. M. Rauhut, B. G. Roberts, and A. M. Semsel, *J. Amer. Chem. Soc.*, 88, 3604 (1966); (d) M. M. Rauhut, D. Sheehan, R. A. Clarke, and A. M. Semsel, *Photochem. Photobiol.*, 4, 1097 (1965); (e) L. J. Bollyky, R. H. Whitman, B. G. Roberts, and M. M. Rauhut, *J. Amer. Chem. Soc.*, 89, 6523 (1967); (f) M. M. Rauhut, L. J. Bollyky, B. G. Roberts, M. Loy, R. H. Whitman, A. V. Iannotta, A. M. Semsel, and R. A. Clarke, *ibid.*, 89, 6515 (1967); (g) L. J. Bollyky, R. H. Whitman, and B. G. Roberts, *J. Org. Chem.*, 33, 4266 (1968); (h) D. R. Maulding, R. A. Clarke, B. G. Roberts, and M. M. Rauhut, *ibid.*, 33, 250 (1968); (i) F. McCapra, *Quart. Rev. Chem. Soc.*, 20, 485 (1966); (j) H. Güsten and E. F. Ullman, *Chem. Commun.*, 28 (1970); (k) M. M. Rauhut and G. W. Kennerly, *Chem. Abstr.*, 74, P26589b (1971).
(2) "Cyalume" Chemical Light (American Cyanamid).
(3) (a) K. R. Kopecky and C. Mumford, *Can. J. Chem.*, 47, 709 (1969); (b) W. H. Richardson and V. F. Hodge, *J. Amer. Chem. Soc.*, 93, 3996 (1971); (c) W. H. Richardson, M. B. Yelvington, and H. E. O'Neal, *ibid.*, 94, 1619 (1972); (d) J. H. Wieringa, J. Strating, H. Wynberg, and W. Adam, *Tetrahedron Lett.*, 169 (1972); (e) N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, 94, 2886 (1972).
(4) (a) P. D. Bartlett and A. P. Schaap, *ibid.*, 92, 3223 (1970); (b) S. Mazur and C. S. Foote, *ibid.*, 92, 3225 (1970); (c) A. P. Schaap and P. D. Bartlett, *ibid.*, 92, 6055 (1970); (d) A. P. Schaap, *Tetrahedron Lett.*, 1757 (1971); (e) T. Wilson and A. P. Schaap, *J. Amer. Chem. Soc.*, 93, 4126 (1971); (f) J.-J. Basselier and J.-P. LeRoux, *C. R. Acad. Sci.*, 270, 1366 (1970); (g) J.-J. Basselier, J.-C. Cherton, and J. Caille, *ibid.*, 273, 514 (1971); (h) G. Rio and J. Berthelot, *Bull. Soc. Chim. Fr.*, 3555 (1971).

(5) Detection of 1 by mass spectral analysis was reported,[6] but this has been subsequently shown to be an artifact.[7]
(6) H. F. Cordes, H. P. Richter, and C. A. Heller, *J. Amer. Chem. Soc.*, 91, 7209 (1969).
(7) J. J. DeCorpo, A. Baronavski, M. V. McDowell, and F. E. Saalfeld, *ibid.*, 94, 2879 (1972).
(8) (a) T. A. Hopkins, H. H. Seliger, E. H. White, and M. W. Cass, *ibid.*, 89, 7148 (1967); (b) W. D. McElroy, H. H. Seliger, and E. H. White, *Photochem. Photobiol.*, 10, 153 (1969).
(9) W. Adam and J.-C. Liu, *J. Amer. Chem. Soc.*, 94, 2894 (1972).
(10) L. J. Bollyky, *ibid.*, 92, 3230 (1970).
(11) H. E. O'Neal and W. H. Richardson, *ibid.*, 92, 6553 (1970).

mechanism, suggests that such calculated activation parameters for **1** should provide a useful guide to conditions under which it may be isolated. Also, the correspondence between the calculated activation parameters for **2a** and **2b** with the reported approximate half-life of **2a**[9] can be made.

Results and Discussion

1,2-Dioxetane-Biradical Thermochemistry. Calculated thermochemical values for the various species in the two-step processes (eq 3 and 4) are given in
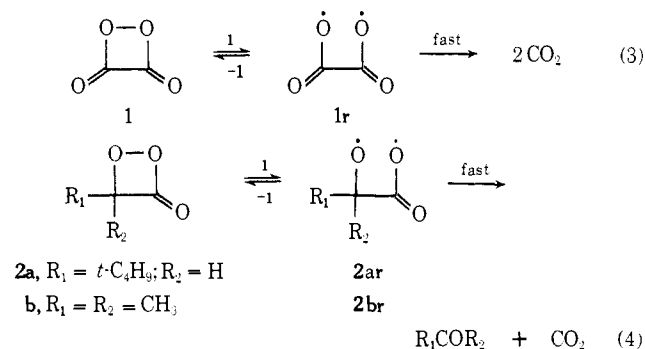

2a, $R_1 = t\text{-}C_4H_9; R_2 = H$ **2ar**
b, $R_1 = R_2 = CH_3$ **2br**

$$R_1COR_2 + CO_2 \quad (4)$$

Table I. Where uncertainties in the thermodynamic

Table I. Thermochemistry of 1,2-Dioxetanes and the Corresponding Biradicals

Species	$S^\circ_{(intrin)}{}^{a,b}$	$\Delta S^\circ_{1,-1}{}^{a,c}$	$\Delta H_f^\circ{}^d$	$\Delta H^\circ_{1,-1}{}^{d,e}$
1	74.5		−74.4	
		2.3		5.0
1r	76.8		−69.4	
2a	104.4		−64.0	
		3.4		10.9
2ar	107.8		−53.1	
2b	86.5		−55.0	
		3.8		9.7
2br	90.3		−45.3	

^{a} eu. ^{b} Intrinsic entropies are $S^\circ(\text{intrin}) = S^\circ(\text{obsd}) + R \ln \sigma/ng_e$. The biradicals are assumed to be singlets, since by spin conservation rules, only singlets can undergo ring closure. The spin degeneracy term (g_e) is then one. The symmetry number and the number of optical isomers are given by σ and n, respectively. $^c \Delta S^\circ_{1,-1} = S^\circ(\text{biradical}) - S^\circ(\text{1,2-dioxetane})$. ^{d} kcal/mol. $^e \Delta H^\circ_{1,-1} = \Delta H_f^\circ(\text{biradical}) - \Delta H_f^\circ(\text{1,2-dioxetane})$.

values exist, the values selected were those which predict maximum stability for the 1,2-dioxetanes. Thus, a strain energy of 26 kcal/mol was used for the 1,2-dioxetane ring (a value previously justified for methyl substituted 1,2-dioxetanes),[11] even though replacement of sp³-hybridized ring carbon atoms by one or two sp²-hybridized carbonyl carbon atoms would be expected to increase the ring strain. For example, strain energies in four-membered hydrocarbon rings are: cyclobutane (26.2 kcal/mol); cyclobutene (29.8 kcal/mol); methylenecyclobutane (28.9 kcal/mol).[12,13] Our intent in selecting values, which give maximum stability for 1,2-dioxetanes **1** and **2**, is to predict the maximum temperatures at which synthesis and isolation of **1** and **2** have a reasonable chance of success.

To obtain the thermodynamic values listed in Table

(12) C. T. Mortimer, "Reaction Heats and Bond Energies," Pergamon Press, New York, N. Y., 1960, p 26.
(13) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

I,[14] several group additivity values not presently reported had to be estimated. For ΔH_f° (**1**) and ΔH_f°(**1r**), the groups whose heats of formation were required are [CO–(CO)(O)] and [CO–(CO)(Ȯ)], respectively. The former group value was obtained from an estimate of the heat of formation of oxalic acid (gas) and the additivity relationship (eq 5). With $\Delta H_f^\circ((COOH)_2)$, gas)

$$\Delta H_f^\circ((COOH)_2, \text{gas}) = 2\Delta H_f^\circ[CO-(CO)(O)] + 2\Delta H_f^\circ[O-(CO)(H)] \quad (5)$$

$= -185.0$ kcal/mol (obtained from $\Delta H_f^\circ((COOH)_2$, solid) $= -198.4$[15] kcal/mol and $\Delta H^\circ((COOH)_2)_{\text{sublimation}} = 13.4$[16] kcal/mol) and [O–(CO)(H)] $= -61.3$[17] kcal/mol along with a gauche interaction (G_0) of 0.5 kcal/mol, one obtains $\Delta H_f^\circ[CO-(CO)(O)] = -31.2$ kcal/mol. The value of $\Delta H_f^\circ[CO-(CO)(Ȯ)]$ was extracted from an estimated heat of formation of the oxalyl radical, $\Delta H_f^\circ(HOOC-COO\cdot) = -127.2$ kcal/mol.[19] This value is based on the assumption that the (COO–H) bond dissociation energy in oxalic acid is the same as that in acetic acid, namely $DH^\circ(CH_3COO-H) = 109.9$ kcal/mol. With the additivity relationship (eq 6) and other known or deduced additivity values as given below, one obtains $\Delta H_f^\circ[CO-(CO)(Ȯ)] = -34.7$ kcal/mol.

$\Delta H_f^\circ(HOOCCOO\cdot)$[19] $= \Delta H_f^\circ[O-(CO)(H)]$[17] $+$
values: -127.2 -61.3
(kcal/mol)

$$\Delta H_f^\circ[CO-(CO)(O)] + \Delta H_f^\circ[CO-(CO)(Ȯ)] \quad (6)$$
values: -31.2
(kcal/mol)

Heats of formation of **2a**, **2b**, and **2ar**, **2br** are also based on two unreported group values. These groups and their estimated values are $\Delta H_f^\circ[C-(CO)(C)_2(O)] = -4.4$ kcal/mol and $\Delta H_f^\circ[C-(CO)(C)_2(Ȯ)] = 10.8$ kcal/mol, respectively. The estimated values were obtained by adding 2.2 kcal/mol to the heat of formation additivities of the groups [C–(C)₃(O)] and [C–(C)₃(Ȯ)] whose reported values are -6.6 and $+8.6$[20] kcal/mol, respectively. These latter groups only differ from the desired groups by a ligand replacement of (C) for (CO). The 2.2 kcal/mol correction comes from a comparison of the heats of formation of several other groups which differ by the same substitution: [CO–(CO)(O)] − [CO–(C)(O)] $= -31.2 - (-33.4) = 2.2$; [CO–(CO)(C)] − [CO–(C)₂] $= -29.2 - [-31.5] = 2.3$ (all in units of kcal/mol). It should be noted that the above group estimates only affect the absolute values of the heats of formation of **2a**, **2b**, and **2ar**, **2br**; they do not affect the kinetic estimates which depend on their heat

(14) The group additivity method was used to calculate the S°(intrinsic) and ΔH_f° values.[13] Thus, the heat of formation of a molecule or biradical is obtained by summing group ΔH_f° values along with ring strain and gauche interactions. Group notation for OC—C(=O)O is, for example, [CO–(CO)(O)].[13]
(15) R. C. Wilhoit and D. Shiao, *J. Chem. Eng. Data*, **9**, 595 (1964).
(16) H. E. O'Neal and B. Kesthelyi, unpublished data.
(17) $\Delta H_f^\circ(CH_3COOH, \text{gas}) = -104.8$[13,18] kcal/mol $= $ [O–(CO)(H)] $+$ [CO–(C)(O)] $+$ [C–(H)₃] $= $ [O–(CO)(H)] $+$ [−33.4][13] $+$ [−10.08],[13] to give [O–(CO)(H)] $= -61.3$ kcal/mol.
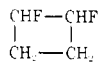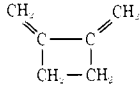(18) R. Keller, "Basic Tables in Chemistry," McGraw-Hill, New York, N. Y., 1967.
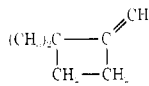(19) $DH^\circ(HOOCCOO-H) = \Delta H_f^\circ(H\cdot) + \Delta H_f^\circ(HOOCCOO\cdot) - \Delta H_f^\circ(HOOCCOOH) = 109.9$ kcal/mol $= (52.1)$[13] $+ \Delta H_f^\circ(HOO-CCOO\cdot) - (-185.0)$, to give $\Delta H_f^\circ(HOOCCOO\cdot) = -127.2$ kcal/mol.
(20) H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, **1**, 221 (1969).
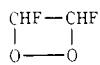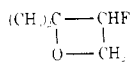
of formation differences (*i.e.*, on $\Delta H^\circ{}_{1,-1}$). It should also be noted that these enthalpy additivity estimates implicitly assume that the [RCOR$_2$CO–H] bond dissociation energy is the same as the (O–H) bond dissociation energy in *tert*-butyl alcohol namely DH$^\circ$-[(CH$_3$)$_3$CO–H] = 105.2 kcal/mol.[21]

Intrinsic entropies of the cyclic peroxides and their corresponding biradicals (Table I) were also estimated by group additivities.[13] To show that the group additivity estimates are reasonable, they are compared in Tables II and III with intrinsic entropies of a number of

Table II. Entropies of 1,2-Dioxetanes **1** and **2b** Estimated by Analogy to Model Compounds and Compared to the Group Additivity Method

Model compounds	S°(intrin)^a	S°(corrected)^a
Model compounds for **1**		
CHF—CHF | | CH$_2$—CH$_2$	76.6^{e,f}	74.3
CH$_2$ CH$_2$ C—C CH$_2$—CH$_2$	75.4^{b,f}	74.4
CHF—CHF | | O——O	74.5^c	74.5
1 (by group additivities)		74.5^d
Model compounds for **2b**		
(CH$_3$)$_2$C—C$^{\text{CH}_2}$ CH$_2$—CH$_2$	87.4^{b,e,f}	
(CH$_3$)$_2$C—CHF O——CH$_2$	86.1^f	85.9
2b (by group additivities)		86.5^d

^{a} eu. ^{b} Corrected for extra double bond torsions (− 0.3 eu each) rocks. ^{c} Calculated from S°(O–CH$_2$–CH$_2$–O) = 65.5 and 4.5 eu increase for each replacement of F for H. ^{d} Assumes [CO–(CO)(O)] = [CO–(C)(O)] and [O–(CO)(O)] = [O–(C)(O)]. ^{e} Corrected for the extra ring entropy in cyclobutane (−1.9 eu). ^{f} Corrected for methylene rocks (− 0.2 eu each).

compounds analogous in structure and molecular weight to **1**, **1r**, **2b**, and **2br**. The intrinsic entropies of compounds with similar structures and molecular weights should be very comparable. That is, rotational and translational entropy contributions will be essentially the same, and vibrational entropies, which are small, will also be very similar. Where obvious differences exist between the model compounds and the species of interest (*i.e.*, **1**, **1r**, **2b**, **2br**) such as "extra" low frequency vibrations, extra internal rotations, or different internal rotational barrier heights, their entropies have been corrected by standard methods[22] to give values (S°(corrected)) that are expected to be closer to those of the desired species. It is clear from the good data correlations of Tables II and III that the group additivity entropies do give very reasonable values of S°(corrected) (*i.e.*, to ±1 eu) for the 1,2-dioxetanes and their corresponding biradicals. Errors as high as ±2

(21) DH$^\circ$[(CH$_3$)$_3$CO–H] = $\Delta H_f{}^\circ$(H·) + $\Delta H_f{}^\circ$(*t*-BuO·) − $\Delta H_f{}^\circ$(*t*-BuOH) = 52.1[13] + [−21.6][13] − [−74.7][13] = 105.2 kcal/mol.
(22) H. E. O'Neal and S. W. Benson, *J. Chem. Eng. Data*, **15**, 266 (1970).

Table III. Entropies of Biradicals **1r** and **2br** Estimated by Analogy to Model Compounds and Compared to the Group Additivity Method

Model Compounds	S°(intrin)^a	S°(corrected)^a
Model compounds for **1r**		
HOOC–COOH	78.6	76.4^b
CF$_2$CH–CF$_2$H	78.2	76.7^c
N$_2$O$_4$	76.9	76.9
1r (by group additivities)	76.8	76.8^{d,e}
Model compounds for **2br**		
(CH$_3$)$_2$C(OH)COOH	94.1	90.6^b
(CH$_3$)$_2$CFHCF$_2$H	92.2	90.7^c
(CH$_3$)$_2$CHNO$_2$	87.7	92.2
2br (by group additivities)	90.3	90.3^{d,e}

^{a} eu. ^{b} Corrected for the internal rotational entropies of the OH groups in the acid, where the rotational barriers are $\sim$17 kcal/mol. ^{c} Corrected for a rotational barrier change from about 4 kcal/mol in fluorocarbons to about 1 kcal/mol in the biradical. ^{d} Entropy group additivities. ^{e} Assumes S°[CO–(O)(CO)] = S°[CO–(O)(C)] = 38.4 eu (calculated from S°(CH$_3$COO·) = 68.8 eu); and that S°[C–(CO)(C)$_2$(O)] = S°[C–(C)$_3$(O)] = −8.9 eu.[20]

eu in the entropy differences (*i.e.*, in $\Delta S^\circ{}_{1,-1}$) only introduce a factor of 2.7 error in estimated A factors and rate constants.

Activation Parameters

The activation energy (E) for the two-step mechanism, as shown in eq 3 and 4, is given by $E = \Delta H^\circ{}_{1,-1} + E_{-1}$, where E_{-1} is the activation energy for closure of the biradical to the 1,2-dioxetane. The value of E_{-1} should depend on the exothermicity of the 1,2-dioxetane-biradical step. A Polanyi relationship between E_{-1} and $\Delta H^\circ{}_{1,-1}$ was previously obtained from data on a series of substituted cyclobutanes which undergo analogous two-step thermal decompositions. That result was $E_{-1} = -0.104\Delta H^\circ{}_{1,-1} + 12.2$.[11] This Polanyi relationship for cyclobutanes predicted a somewhat larger value of E_{-1} (10.6 kcal/mol) than that calculated from the experimental activation parameters of the trimethyl-1,2-dioxetane decomposition ($E_{-1} = 8.5$ kcal/mol).[23] A "best" value for E_{-1} in the reactions considered here, then, is 2.1 kcal/mol lower than those predicted from the Polanyi relationship. However we have used the Polanyi relationship value of 11.7, 11.1, and 11.2 kcal/mol for the E_{-1} values of **1**, **2a**, and **2b**, since these values give an upper limit for the overall activation energies E, and therefore an upper limit estimate of the 1,2-dioxetane stabilities. As stated previously, this will reflect the most optimistic hopes of isolating **1**, **2a**, and **2b**.

The entropy of activation for the two-step process is given by $\Delta S^\ddagger = \Delta S^\circ{}_{1,-1} + \Delta S_{-1}{}^\ddagger + R \ln (\sigma n^\ddagger / \sigma^\ddagger n)$,[25] where the last term is zero. Thermochemical analysis of the kinetics of cyclobutane reactions, relative to the biradical mechanism, has shown that the activation entropies ($\Delta S_{-1}{}^\ddagger$) for 1,4-biradical cyclizations to four-membered rings can be equated to the entropy of internal rotation about the C$_2$–C$_3$ bond in the biradical. This is the reaction coordinate for cyclization. The

(23) See ref 11, which employs the observed activation parameters of trimethyl-1,2-dioxetane that were kindly supplied by Professor Kopecky.[24]
(24) See also K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969).
(25) σ, n and $\sigma^\ddagger$, $n^\ddagger$ are the symmetry number and number of optical isomers of the reactant and transition state, respectively. The ratio ($\sigma n^\ddagger / \sigma^\ddagger n$) is the reaction path degeneracy.

Table IV. Calculated Maximum Activation Parameters and Related Quantities for the Thermal Decomposition of **1**, **2b**, and **2b**

1,2-Dioxetane	$E_{-1}{}^a$	$\Delta S^{\pm}_{-1}{}^b$	E^a	$\Delta S^{\pm b}$	Log A	k^c	$\tau = 1/k^d$
1	11.7	-6.1	16.7	-3.8	12.4	1.9	0.54
2a	11.1	-6.3	22.0	-2.9	12.6	4.0×10^{-4}	2500 (42 min)
2b	11.2	-5.9	20.9	-2.1	12.8	4.0×10^{-3}	250 (4.2 min)

^{a} kcal/mol. ^{b} eu. ^{c} Calculated from the activation parameters at 27°, sec^{-1}. ^{d} Lifetime calculated at 27°, sec.

rotational entropies for **1r**, **2ar**, and **2br** are based on the entropies of rotation in the corresponding hydrocarbon biradicals.[26] Thus, by procedures given previously[26,27]

$$\Delta S_{-1}{}^{\pm}(\mathbf{1r} \longrightarrow \mathbf{1}) = -S°(i\text{-Pr} \xrightarrow{\;a\;} i\text{-Pr})_{v=4\ \text{kcal}} =$$
$$-6.1\ \text{eu}$$

$$\Delta S_{-1}{}^{\mp}(\mathbf{2ar} \longrightarrow \mathbf{2a}) = -S°(i\text{-Pr} \xrightarrow{\;a\;} \infty)_{v=6\ \text{kcal}} =$$
$$-6.3\ \text{eu}$$

$$\Delta S_{-1}{}^{\pm}(\mathbf{2br} \longrightarrow \mathbf{2b}) =$$
$$-S°(t\text{-Bu} \xrightarrow{\;a\;} i\text{-Pr})_{v=7\ \text{kcal}} = -5.9\ \text{eu}$$

A summary of the estimated maximum activation parameters for **1**, **2a**, and **2b** are given in Table IV. The values in Table IV represent *maximum* activation parameters and thus maximum lifetimes. The maximum calculated stabilities of **1**, **2a**, and **2b** may be compared to that of 3,3-dimethyl-1,2-dioxetane (**4**). The

$$\begin{array}{c} \text{O—O} \\ |\quad\ | \\ (CH_3)_2C\text{—}CH_2 \end{array}$$
4
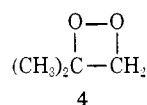
observed lifetime of **4** at 27° is 9.4 hr in carbon tetrachloride solution, a value which is in good agreement with our calculated activation parameters.[3c] The calculated rate coefficients for 1,2-dioxetanes containing sp^2 carbonyl carbons in the ring clearly predict lower stabilities than those where all the ring carbons are sp^3 hybridized. This prediction is substantiated by the recent report of the isolation of **2a**, where the approximate lifetime at room temperature is 5–8 min.[9] Our calculations estimate a *maximum* lifetime of **2a** to be 42 min, which is in good agreement for this type of calculation. The agreement between observed and calculated half-lives for **2a** places added confidence in the estimates of

activation parameters for **1** and **2b**. As an arbitrary guide, one may assume that 2 hr is a sufficient lifetime for isolation and spectral characterization. For a lifetime of 2 hr, temperatures of -48 and 0° are required for **1** and **2b**, respectively, based on the calculated activation parameters.

Although the acceptor (A) may be intimately involved in the decomposition of **1** (eq 1) in the oxalate–hydrogen peroxide reaction, one can determine whether or not it is possible to produce an excited state carbon dioxide molecule from **1**, which transfers energy to A. With the $\Delta H_f°$ value of **1** from Table I and the $\Delta H_f°$ for carbon dioxide,[13] the heat of reaction for **1** to give two carbon dioxide molecules is calculated to be -112.9 kcal/mol. The maximum available energy that can be transferred to a carbon dioxide molecule in the decomposition of **1** is $(E - \Delta H_r) = 16.7 + 112.9 = 130$ kcal.[1k,11] This is sufficient energy to obtain a triplet carbon dioxide molecule ($\sim$110 kcal),[28] but not a singlet species ($\sim$141 kcal).[28] For symmetrically substituted 1,2-dioxetanes, where there is sufficient energy available for excitation of one of the carbonyl species, but not both, it is reported that one excited state carbonyl species is produced per 1,2-dioxetane decomposed.[3e,4e] Presumably this would also occur with **1** if triplet carbon dioxide can be produced without the intervention of the singlet species. Direct formation of triplet acetone from tetramethyl-1,2-dioxetane was recently reported.[3e] This result can be accommodated by the two-step mechanism, where the initially formed biradical is a singlet (a requirement for ring closure back to the 1,2-dioxetane). Spin conversion to a triplet biradical (non-rate-determining) could then occur with subsequent decomposition to triplet and ground state (singlet) carbonyl species.

(26) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).
(27) H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 423 (1970).

(28) R. S. Mulliken, *Can. J. Chem.*, **36**, 10 (1958).