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Determination of the Equilibrium Constant and Thermodynamic Parameters for the Reaction of Pentadienyl Radicals with O_2

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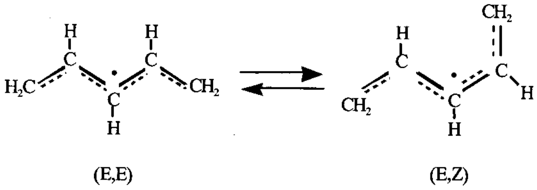
The reaction of pentadienyl radicals (C_5H_7) with O_2 has been studied by a combination of pulsed laser photolysis and photoionization mass spectrometry. These radicals were generated either by the photolysis of 1,3-pentadiene or by a two step process, photolyzing carbon tetrachloride to form Cl atoms, which then abstracted a hydrogen atom from 1,4-pentadiene. The equilibrium between pentadienyl radicals, O_2 and pentadienylperoxy radicals could be observed over the temperature range 268−308 K. An analysis of the time-dependent signal of pentadienyl radicals was used to evaluate the equilibrium constant. From the temperature dependence of the equilibrium constant, the enthalpy change for the reaction $C_5H_7 + O_2 \rightarrow C_5H_7O_2$ was found to be 56 ± 5 kJ mol^{-1}. The C−O bond energy in the $C_5H_7{-}O_2$ adduct is weaker than those of allyl-type peroxy radicals. Possible values of the heats of formation of C_5H_7 and $C_5H_7{-}O_2$ radicals and the resonance stabilization energy of the C_5H_7 radical are discussed.

Introduction

In 1981, Ruiz et al.[1] reported the direct observation of the equilibrium between allyl radicals, C_3H_5, O_2, and allylperoxy radicals. Subsequent studies observed the equilibria for several other hydrocarbon radicals (CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9, and benzyl) with O_2 using similar methods.[2−5]

Recently, we reported[6] the observation of the equilibrium between cyclohexenyl radicals, O_2, and cyclohexenylperoxy radicals at 361 K. The cyclohexenyl radical can be thought of as a cyclic allyl-type radical. The C−O bond energy in the cyclohexenylperoxy radical, 80 kJ mol^{-1}, is similar to the C−O bond energy in the allylperoxy radical, 76 kJ mol^{-1}. Both of these are much weaker than the C−O bond energies of alkylperoxy radicals, which are in the range 135−155 kJ mol^{-1}. These weak bonds can be attributed to the loss of the allylic resonance stabilization energy (RSE) when the C−O single bond is formed.

In the case of pentadienyl radicals (C_5H_7), it has been suggested [7−10] that the radical can exist in the *E*,*E* or the *E*,*Z* structure and that both conformers are at equilibrium.



(1)

The single unpaired electron is expected to delocalize over all five carbon atoms. This delocalization is more extensive than that for cyclohexenyl or allyl radicals (over three carbon atoms). The RSE of the pentadienyl radical, which has been reported to be 64,[11] 77,[12] and 71[13] kJ mol^{-1} by experiment and 82 kJ mol^{-1} by ab intio calculation,[10] is larger than the RSE of the allyl radicals (59−61 kJ mol^{-1}).[14] It is then of interest to study the equilibrium and the C−O bond energy of RO_2 for this radical ($R^{\bullet}$) with a larger RSE.

In the present study, the direct observation of the equilibrium between pentadienyl radicals, O_2, and pentadienylperoxy radicals will be reported. The study was carried out by combining laser flash photolysis to generate the C_5H_7 radicals and photoionization mass spectrometry to detect them. The equilibrium constant has been measured at various temperatures. From these measurements, the C−O bond energy of pentadienylperoxy radicals can be evaluated.

Experimental Section

The experimental setup used in this work is similar to that described previously.[6] The radical precursors and O_2 were introduced into a tubular Pyrex reactor (13 mm i.d.) with N_2 as the carrier gas. Pulsed 193 nm radiation from an ArF excimer laser (Lambda Physik, LPX 120) was directed along the axis of the reactor. The gas in the reactor was sampled through an orifice (diameter 0.3 mm) located in the wall of the reactor, and the time dependence of the radical concentrations was recorded directly by photoionization mass spectrometry. Schematic diagrams of the apparatus have been shown in previous papers.[15−17]

Pentadienyl radicals were generated by pulsed laser photolysis of 1,3-pentadiene at 193 nm, reaction 2, and also by photolysis of carbon tetrachloride to give chlorine atoms, which then

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reacted with 1,4-pentadiene to form pentadienyl radicals.

$$\mathrm{CH_2{=}CH{-}CH{=}CH{-}CH_3} + h\nu_{193} \rightarrow \mathrm{C_5H_7 + H} \tag{2}$$

$$\mathrm{CCl_4} + h\nu_{193} \rightarrow \mathrm{Cl + CCl_3} \tag{3a}$$

$$\rightarrow \mathrm{2Cl + CCl_2} \tag{3b}$$

$$\mathrm{CH_2{=}CH{-}CH_2{-}CH{=}CH_2 + Cl} \rightarrow \mathrm{C_5H_7 + HCl} \tag{4a}$$

$$\rightarrow \text{other products} \tag{4b}$$

The resulting pentadienyl radicals were ionized by the resonance line from a microwave-powered Xe lamp having a sapphire window (8.44 eV).

The ion signals were recorded as a function of time with a Lecroy 9400A digital storage oscilloscope for 20 ms following each laser pulse. Signals were transferred to a personal computer after each laser pulse and were discriminated, counted, and accumulated for typically 2−3 × 10^4 laser pulses before analysis. Typical laser power and repetition rate used are 1 × 10^{15} photon cm^{-2} pulse^{-1} and 10−15 Hz, respectively. At the repetition rate of 10−15 Hz, the flow velocity was high enough to completely replace the gas in the reaction tube between laser pulses.

Typical partial pressures used were 0.1 mTorr (1,3-pentadiene), 0.5 mTorr (1,4-pentadiene), and 5 mTorr (CCl_4) all in N_2 (6 Torr). The stated purities were as follows: N_2 (Nippon Sanso, 99.9995%), O_2 (Nippon Sanso, 99.99%), 1,3-pentadiene (Wako, 98%), 1,4-pentadiene (Wako, 98%), and CCl_4 (Wako, >98%). From the absorption cross section at 193 nm of 1,3-pentadiene ($\sigma_{193} = 3 \times 10^{-17}$ cm^2), 1,4-pentadiene ($\sigma_{193} = 8 \times 10^{-18}$ cm^2), and CCl_4 ($\sigma_{193} = 8.8 \times 10^{-19}$ cm^2), the initial concentration of parent molecules, and the laser power, the initial concentration of pentadienyl radicals was estimated to be approximately 10^{11} molecules cm^{-3}. Preliminary experiments (variation of the initial concentration of 1,3-pentadiene, 1,4-pentadiene, and CCl_4 and the laser power) indicated that radical−radical reactions made no significant contribution to radical loss for the radical concentrations used.

The reaction zone of the flow reactor could be heated or cooled. For low temperatures, cold methanol was circulated through a jacket surrounding the flow reactor by using a refrigerated circulating bath (Neslab ULT 80). For higher temperatures, hot water was circulated from a high-temperature bath (Exacal EX-250 HT). Before each run, the temperature was measured with a copper−constantan thermocouple suspended in the center of the flow reactor; this was removed for kinetic experiments. The temperature uniformity was ±1 K.

Results and Discussion

Formation and Detection of Pentadienyl Radicals. Ion signals at m/z = 67, 68, and 69 were detected following the photolysis of each of the following mixtures: 1,3-pentadiene/N_2; 1,4-pentadiene/N_2; 1,3-pentadiene/CCl_4/N_2; and 1,4-pentadiene/CCl_4/N_2. The mass spectra shown in Figure 1 are the difference spectra between the signal with irradiation and without irradiation. The dashed lines in Figure 1 show spectra observed in the absence of CCl_4, whereas the solid lines show spectra measured in the presence of CCl_4. Because the Xe lamp (8.44 eV) was used for photoionization, parent peaks at m/z = 68 were not observed for 1,3-pentadiene (IP = 8.6 eV)[18] and 1,4-pentadiene (IP = 9.6 eV)[19] without laser irradiation.

Signals at m/z = 67 were observed in each of the above systems, and these were assigned to pentadienyl radicals, because the decay profiles were quite similar in the presence of O_2. Also, these signals increased with laser power. As is shown by the dashed line spectra in Figure 1, the pentadienyl radical can be produced by direct photodissociation of both 1,3- and 1,4-pentadiene (reactions 2 and 5a) in competition with processes producing other fragments.

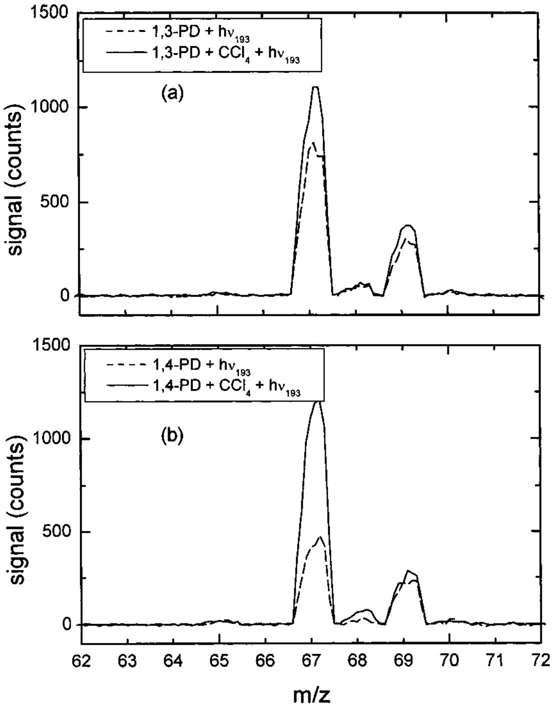

Figure 1. Mass spectra of the ion signal in the following systems: (a) 1,3-pentadiene + $h\nu$ (193 nm) and CCl_4 + 1,3-pentadiene + $h\nu$ (193 nm); (b) 1,4-pentadiene + $h\nu$ (193 nm) and CCl_4 + 1,4-pentadiene + $h\nu$ (193 nm). At each point, the signal was counted during 2 ms alternatively just before and just after each laser shot, and the difference signal was accumulated for a total of 200 shots at each mass number (10 points per unit mass number). Conditions: T = 298 K, P = 5.9 Torr (buffer gas, N_2), ArF laser fluence = 1.2 × 10^{15} photons cm^{-2}, (a) [1,3-pentadiene] = 2.3 × 10^{12} molecules cm^{-3}, [CCl_4] = 1.7 × 10^{14} molecules cm^{-3}, (b) [1,4-pentadiene] = 1.7 × 10^{13} molecules cm^{-3}, [CCl_4] = 1.7 × 10^{14} molecules cm^{-3}.

$$\mathrm{CH_2{=}CH{-}CH_2{-}CH{=}CH_2} + h\nu_{193} \rightarrow \mathrm{C_5H_7 + H} \tag{5a}$$

$$\rightarrow \text{other products} \tag{5b}$$

When the same amount of CCl_4 was added to both systems (1,3-pentadiene + $h\nu$ and 1,4-pentadiene + $h\nu$), the signal at m/z = 67 increased for both. These results show that hydrogen atom abstraction by a Cl atom can occur in both 1,3- and 1,4-pentadiene, reactions 6 and 4, respectively.

$$\mathrm{CH_2{=}CH{-}CH{=}CH{-}CH_3 + Cl} \rightarrow \mathrm{C_5H_7 + HCl} \tag{6}$$

As is shown by the solid line spectra in Figure 1, the increase in the signal at m/z = 67 was much larger for the case of 1,4-pentadiene. Consequently, we opted for the photolysis of 1,3-pentadiene, reaction 2, and the photolysis of a mixture of 1,4-pentadiene/CCl_4/N_2, reaction 4, to generate pentadienyl radicals for the equilibrium studies.

The small signals at m/z = 68 (about 5% of the m/z = 67 signal) in Figure 1 might originate from the natural abundance of ^{13}C in the pentadienyl radical. The signal at m/z = 69 probably comes from photoionization of pentenyl radicals (C_5H_9) which can be produced by the addition of a hydrogen atom, produced in reactions 2 and 5, to another 1,3- or 1,4-

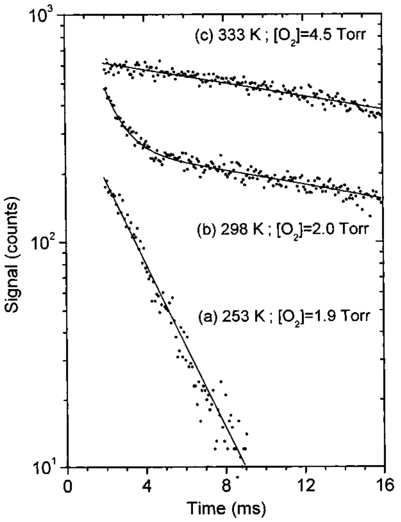

Figure 2. Pentadienyl radicals temporal profiles for three different conditions: (a) 253 K, $[O_2] = 1.9$ Torr (7.2×10^{16} molecules cm^{-3}), [1,3-pentadiene] = 0.07 mTorr (2.7×10^{12} molecules cm^{-3}); (b) 298 K, $[O_2] = 2.0$ Torr (6.5×10^{16} molecules cm^{-3}), [1,3-pentadiene] = 0.08 mTorr (2.6×10^{12} molecules cm^{-3}); (c) 333K, $[O_2] = 4.5$ Torr (1.3×10^{17} molecules cm^{-3}), [1,3-pentadiene] = 0.12 mTorr (3.5×10^{12} molecules cm^{-3}). The total pressure ($O_2 + N_2$ mostly) is 1.9×10^{17} molecules cm^{-3} for each run.

pentadiene.

$$C_5H_8 + H + M \rightarrow C_5H_9 + M \qquad (7)$$

Reaction 7 is supported by the observation that the signal at $m/z = 69$ did not appear immediately after photolysis but grew up linearly. Because the ionization potentials of the pentadienyl and pentenyl radicals have been reported to be 7.3−7.8[20] and 7.1−7.7[21] eV, respectively, both can be photoionized by the Xe resonance line (8.44 eV).

Decay Profiles of Pentadienyl Radicals. Figure 2 shows the time profiles of the pentadienyl ion signals in the presence of O_2 when mixtures of 1,3-pentadiene/O_2/N_2 were photolyzed at three different temperatures.

At 253 K (Figure 2a), a rapid single-exponential decay is observed when O_2 is present. This decay can be explained by reaction 8:

$$C_5H_7 + O_2 + M \rightarrow C_5H_7O_2 + M \qquad (8)$$

Because the signal follows a single-exponential decay, the rate law of the process is given by eq 9.

$$[C_5H_7] = [C_5H_7]_0 \exp(-k't) \qquad (9)$$

Here, $[C_5H_7]_0$ stands for the initial concentration of pentadienyl radicals and k' represents the sum of decay rates of the radical:

$$k' = k_8[O_2] + k_{w1} \qquad (10)$$

In this equation, k_8 is the effective rate constant for reaction 8, which may be a function of total pressure, and k_{w1} represents other first order loss processes (probably loss on the wall). In the measurement shown in Figure 2a, the value for k' is 430 s^{-1}, that for k_{w1} (measured in the absence of O_2) is 100 s^{-1}, and the concentration of O_2 and total pressure ($O_2 + N_2$ mostly) are 7.2×10^{16} and 1.9×10^{17} molecules cm^{-3}, respectively. The value of k_8 can be calculated as 4.6×10^{-15} cm^3 molecule^{-1} s^{-1} for these particular conditions. The rate constant value of k_8 is surprisingly slow. The measured value of k_8 did not change significantly when increasing the total pressure from 1.1×10^{17} to 2.3×10^{17} molecules cm^{-3}.

When elevating the temperature to 333 K (Figure 2c), a very slow decay of the signal was observed (39 s^{-1}). Because the decay rate was then independent of the pressure of O_2 (4.5 Torr of O_2 was added in the case of Figure 2c), this decay is assigned to the rate of the wall-loss process (k_{w1}) at 333 K. This means that the reverse of reaction 8, reaction −8, becomes fast, so that little net reaction of C_5H_7 with O_2 occurs.

$$C_5H_7 + O_2 + M \leftarrow C_5H_7O_2 + M \qquad (-8)$$

At 298 K (Figure 2b), the signal follows a double-exponential decay. This phenomenon was observed at temperatures between 268 and 308 K and can be explained as follows: As pentadienyl radicals react with O_2, the peroxy radical concentration increases until its thermal decomposition back to pentadienyl + O_2 (k_{-8}) just balances the forward rate ($k_8[O_2]$). At longer reaction times, there is only a slow decay due to the wall-loss processes.

Analysis of the Double Exponential Decay. Over the temperature range from 268 to 308 K the decay profile of the pentadienyl radical is governed by reactions 8 and −8 and the wall-loss processes of pentadienyl radicals (k_{w1}) and pentadienylperoxy radicals (k_{w2}). The analysis of rate equations of this system has been described in the previous paper[6] and also by Benson.[22] Briefly, the concentration of the pentadienyl radical [R] and the pentadienylperoxy radical $[RO_2]$ will be given by the coupled equations

$$\frac{d[R]}{dt} = -(k_8[O_2] + k_{w1})[R] + k_{-8}[RO_2] \qquad (11)$$

$$\frac{d[RO_2]}{dt} = k_8[R][O_2] - (k_{-8} + k_{w2})[RO_2] \qquad (12)$$

Because the boundary conditions for [R] and $[RO_2]$ are $[R] = [R]_0$, the initial concentration of pentadienyl radical at $t = 0$, and $[RO_2] = 0$ at $t = 0$, the solutions to the above two differential equations are

$$[R] = A \exp(-\lambda_1 t) + B \exp(-\lambda_2 t) \qquad (13)$$

$$[RO_2] = C\{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\} \qquad (14)$$

The constants A, B, λ_1, and λ_2 can be determined for various O_2 pressures and temperatures by fitting the double exponential decay profiles of pentadienyl ion signals to eq 13. The values of k_8, k_{-8}, and $K_{eq} = k_8/k_{-8}$ were obtained from the fitting parameters A, B, λ_1, and λ_2 according to eqs 15−17.

$$k_8 = \frac{A(\lambda_1 - k_{w1}) + B(\lambda_2 - k_{w1})}{(A + B)[O_2]} \qquad (15)$$

$$k_{-8} = \frac{AB(\lambda_1 - \lambda_2)^2}{(A + B)\{A(\lambda_1 - k_{w1}) + B(\lambda_2 - k_{w1})\}} \qquad (16)$$

$$K_{eq} = \frac{\{A(\lambda_1 - k_{w1}) + B(\lambda_2 - k_{w1})\}^2}{AB(\lambda_1 - \lambda_2)^2[O_2]} \qquad (17)$$

The values of k_{w1} were measured independently in the absence of O_2 for each case. The results are summarized in Table 1. Error limits shown for A, λ_1, B, λ_2, and k_{w1} represent 2 standard deviations derived from the least-squares fitting of the plots.

TABLE 1: Conditions and Results of Experiments to Measure the Equilibrium Constant for the Reaction $C_5H_7 + O_2 \rightleftarrows C_5H_7O_2$[a]

T (K)	O_2 (Torr)	A	λ_1	B	λ_2	k_{w1} (s^{-1})	k_{w2} (s^{-1})	k_8 (10^{-15} cm^3 $molecule^{-1}$ s^{-1})	k_{-8} (s^{-1})	K_{eq} (10^{-16} cm^3 $molecule^{-1}$)
(System 1,3-Pentadiene/$h\nu_{193}$)										
268	0.0	170 ± 6				110 ± 6				
	3.9	817 ± 110	758 ± 68	18 ± 8	50 ± 38		48	4.49	16.7	2.69 ± 1.29
278	0.0	416 ± 12				101 ± 3				
	3.9	1416 ± 182	766 ± 76	67 ± 20	36 ± 31		33	4.70	36.4	1.30 ± 0.45
288	0.0	386 ± 11				98 ± 3				
	4.1	1477 ± 192	803 ± 84	138 ± 22	28 ± 17		21	4.63	73.4	0.63 ± 0.14
298	0.0	667 ± 17				112 ± 3				
	2.0	1111 ± 74	548 ± 50	261 ± 26	33 ± 8		6	5.04	124.6	0.40 ± 0.06
	3.1	1278 ± 120	806 ± 66	255 ± 16	44 ± 6		26	5.53	144.5	0.38 ± 0.04
	4.0	1423 ± 146	955 ± 78	252 ± 14	40 ± 5		24	5.40	153.9	0.35 ± 0.04
308	0.0	444 ± 13				96 ± 3				
	4.2	1308 ± 261	1194 ± 172	432 ± 20	37 ± 6		16	6.17	308.1	0.20 ± 0.04
(System 1,4-Pentadiene /CCl_4 /hν_{193})										
273	0.0	368 ± 13				62 ± 3				
	3.6	927 ± 120	741 ± 82	35 ± 16	49 ± 42		48	5.10	25.7	1.99 ± 1.00
278	0.0	424 ± 13				65 ± 3				
	2.9	495 ± 49	599 ± 70	29 ± 13	46 ± 38		45	5.04	31.8	1.58 ± 0.78
	3.7	785 ± 188	922 ± 126	36 ± 9	53 ± 25		52	6.41	38.7	1.66 ± 0.58
283	0.0	442 ± 14				66 ± 3				
	2.6	577 ± 56	540 ± 66	50 ± 17	36 ± 28		33	4.86	43.0	1.13 ± 0.44
	3.8	663 ± 154	817 ± 150	49 ± 18	43 ± 40		41	5.36	55.0	0.97 ± 0.44
288	0.0	598 ± 16				66 ± 3				
	3.0	785 ± 150	743 ± 108	90 ± 16	53 ± 16		51	6.13	72.5	0.84 ± 0.23
	3.9	1147 ± 230	772 ± 150	111 ± 40	24 ± 40		20	4.95	70.3	0.71 ± 0.31
293	0.0	445 ± 10				58 ± 2				
	3.7	497 ± 70	690 ± 98	94 ± 13	46 ± 12		43	4.35	105.0	0.41 ± 0.08
	3.3	736 ± 106	684 ± 98	124 ± 16	48 ± 12		47	4.87	93.2	0.52 ± 0.10
298	0.0	328 ± 8				72 ± 3				
	2.0	537 ± 70	475 ± 102	203 ± 40	46 ± 14		35	4.31	128.6	0.33 ± 0.09
303	0.0	367 ± 9				74 ± 3				
	2.2	373 ± 76	522 ± 148	205 ± 30	48 ± 12		32	4.05	183.7	0.22 ± 0.06
	3.2	760 ± 188	735 ± 146	280 ± 23	54 ± 7		46	4.63	191.0	0.24 ± 0.07

[a] All runs were at a total pressure of about 6.0 Torr, with N_2 as a carrier gas. The laser fluence intensity was approximately 1.2×10^{15} photons cm^{-2}, and the pentadienyl concentration was about 10^{11} molecules cm^{-3}. The error limits for the parameters A, λ_1, B, and λ_2 represent 2 standard deviations.The uncertainty of the values for K_{eq} are estimated from the standard deviations of A, λ_1, B, λ_2, and k_{w1}.

The estimated uncertainties of the values for K_{eq} are calculated from the relative errors in A, λ_1, B, λ_2, and k_{w1} by propagation of errors.

It should be noted that the values for both k_8 and k_{-8} are unusually small for a free-radical−oxygen reaction. This could be caused by an energy barrier in the entrance channel; however, there is very little dependence of k_8 on temperature, which says that there cannot be a significant barrier. Because reaction 8 is a three body reaction, it could be slow if it were far from the high pressure limit in these experiments. However, that seems unlikely for such a large complex. Also a doubling of the total pressure did not change the measured value of k_8. At the present time, we have no good explanation for the observed small rate constants.

Determination of Thermochemical Parameters. The rate data shown in Table 1 can be employed to calculate K_p ($= k_8/(k_{-8}RT)$), and hence ΔH^0_{298} and ΔS^0_{298} for reaction 8 by plotting the left-hand side of eq 18 against the reciprocal of absolute temperature.[23]

$$\ln K_p - \frac{\Delta C_p}{R}\left\{\ln\left(\frac{T}{298}\right) - \frac{T-298}{T}\right\} = -\frac{\Delta H^0_{298}}{RT} + \frac{\Delta S^0_{298}}{R} \quad (18)$$

This treatment assumes that ΔC_p for reaction 8 is independent of temperature. Because the value for ΔC_p (1 J mol^{-1} K^{-1} estimated by Benson's group additivity methods[23]) is quite small, the term $(\Delta C_p/R)[\ln(T/298) - (T - 298)/T]$ is less than 0.01% of the values for ln K_p, so this approximation should be valid.

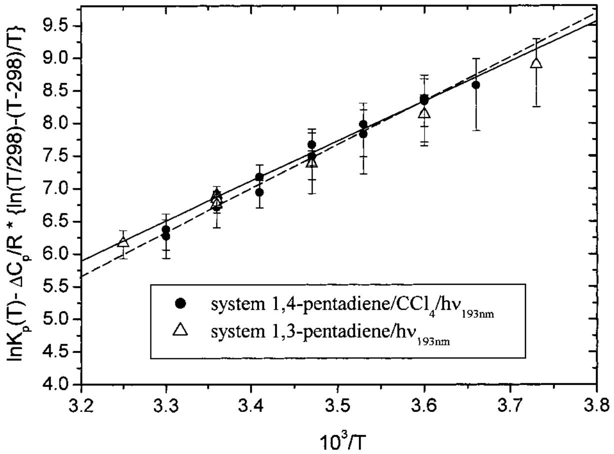

Figure 3. The plot of ln $K_p(T) - (\Delta C_p/R)[\ln(T/298) - (T - 298)/T]$ against $1/T$. The straight line represents a least-squares fit through all of the plotted data. The solid line represents the second-law least-squares fit, and the dashed line is the third-law fit as described in the text.

Figure 3 shows the experimental data plotted according to eq 18. From the slope and intercept of the linear weighted least-squares line (solid line), the following values are calculated for reaction 8:

$$\Delta H^0_{298} = -50 \pm 4 \text{ kJ mol}^{-1} \quad (19)$$

$$\Delta S^0_{298} = -112 \pm 12 \text{ J mol}^{-1} \text{ K}^{-1} \quad (20)$$

Thermochemical parameters calculated by group additivity methods[23,24] for C_5H_7 and $C_5H_7O_2$ radicals are listed in Table

TABLE 2: Thermochemical Parameters for the Reaction $C_5H_7 + O_2$ Calculated by Group Additivity Methods

O_2, R, RO_2	ΔH_f^0(298 K) (kJ mol^{-1})	S^0(298 K) (J mol^{-1} K^{-1})	C_p^0(298 K) (J mol^{-1} K^{-1})
O_2	0	205	29
C_5H_7 (C−C−C−C−C)$^\bullet$	204[a]	321[b]	97[b]
$C_5H_7O_2$(a)[c] C═C−C(OO$^\bullet$)−C═C	153[d]	402[d]	127[d]
$C_5H_7O_2$(b)[c] C═C−C═C−C(OO$^\bullet$)	149[e]	394[f]	127[f]

reaction	ΔH^0 (298 K) (kJ mol^{-1})	ΔS^0(298 K) (J mol^{-1} K^{-1})	ΔC_p^0(298 K) (J mol^{-1} K^{-1})
$C_5H_7 + O_2 \rightarrow C_5H_7O_2$ (a)	−51	−124	1
$C_5H_7 + O_2 \rightarrow C_5H_7O_2$ (b)	−55	−132	1

[a] GAV of $C^\bullet-(C_d)_2(H)$ for ΔH (= 80 kJ mol^{-1}) from Dilling.[26] [b] $C^\bullet-(C)(C_d)$ (H) is used in place of $C^\bullet-(C_d)_2(H)$ for S (= 29.4 J mol^{-1} K^{-1}) and C_p (= 19.2 J mol^{-1} K^{-1}). [c] GAV of $O-(C)(O^\bullet)$ for ΔH (= 59.4 kJ mol^{-1}), S (= 150.5 J mol^{-1} K^{-1}), and C_p (= 29.6 J mol^{-1} K^{-1}) from Stein.[24] [d] $C-(C)_2(H)(O)$ is used in place of $C-(C_d)_2(H)(O)$ for ΔH (= −30.1 kJ mol^{-1}), S (= −46.0 J mol^{-1} K^{-1}), and C_p (= 20.1 J mol^{-1} K^{-1}). [e] GAV of $C-(C_d)(H)_2(O)$ for ΔH (= −28.9 kJ mol^{-1}) from Cohen and Benson.[27] [f] $C-(C)(H)_2(O)$ is used in place of $C-(C_d)(H)_2(O)$ for S (= 41.0 J mol^{-1} K^{-1}) and C_p (= 20.9 J mol^{-1} K^{-1}).

2.[25] Because there is no group additivity ΔH_f^0 value for $C-(C_d)_2(H)(O)$, the value for the group $C-(C)_2(H)(O)$ was used. Also for the ΔS^0_{298} value of the group $C-(C_d)(H)_2(O)$, the group value of $C-(C)(H)_2(O)$ was used. As is shown in Table 2, two structures (a and b) can be considered for $C_5H_7O_2$ radicals; structure a has the C−O bond at the middle carbon, and structure b has it at the end carbon. The estimated thermodynamic parameters shown in Table 2 can be used to calculate an equilibrium constant for the reaction

$$C_5H_7O_2\ (a) \rightleftarrows C_5H_7O_2\ (b) \tag{21}$$

For the temperatures used in this study, the calculated equilibrium constant[28] is close to 2, meaning that approximately 67% of the $C_5H_7O_2$ radicals should have the linear structure of b.

The thermodynamic values derived above from the experimental equilibrium constants agree moderately well with the group additivity estimates for the reaction forming $C_5H_7O_2$ (b): −50 vs −55 kJ mol^{-1} for ΔH^0_{298} and −112 vs −132 J mol^{-1} k^{-1} for ΔS^0_{298}. However, because of the long extrapolation to $1/T$ required by this second-law method, the resulting ΔS^0_{298} is prone to serious error.

It has been suggested[2−5] that a better value for ΔH^0_{298} can be derived by using the third-law method. A least squares line that is constrained to have an intercept of (−132 J mol^{-1} k^{-1})/R still gives a good fit to the experimental data, as shown by the dashed line in Figure 3 and results in a ΔH^0_{298} of −56 ± 5 kJ mol^{-1}, where the indicated error represents 95% confidence limits. This seems to be in excellent agreement with the group additivity estimate in Table 2. However, as described before,[25] the value of $S^0_{298}(C_5H_7)$ = 321 J mol^{-1} K^{-1} in Table 2 was calculated by the assumption that the group additivity S^0_{298} value for $C^\bullet-(C_d)_2(H)$ is nearly equal to that for $C^\bullet-(C)(C_d)(H)$. It is likely that the value of $C^\bullet-(C_d)_2(H)$ is overestimated by such an assumption.[29] Two ab initio calculations on the structure and vibrational frequencies of pentadienyl radicals have been reported.[30,31] The S^0_{298} values of the C_5H_7 calculated from the results of ab initio calculations are about 9 J mol^{-1} K^{-1} smaller[32] than that shown in Table 2. When the value of 312 J mol^{-1}K^{-1} is used for the S^0_{298} of the C_5H_7 and (−123 J mol^{-1} K^{-1})/R is used as an intercept of Figure 3, the ΔH^0_{298} value will change to −53 ± 4 kJ mol^{-1}. Thus, if ab initio calculations for these peroxy radicals become available, so that a better estimate for ΔS^0_{298} can be made, this third-law calculation should be repeated.

Because third-law values are more likely to be correct, we propose the following error limit (±) for the ΔH^0_{298} value of reaction 8 at this stage:

$$\Delta H^0_{298} = -56 \pm 5 \text{ kJ mol}^{-1} \tag{22}$$

TABLE 3: Values of RSE in R and the C−O BDE of RO_2

R	RSE [ref] (kJ mol^{-1})	C−O BDE of RO_2 [ref] (kJ mol^{-1})	RSE+BDE (kJ mol^{-1})
methyl	0	136 ± 3 [2]	136 ± 3
ethyl	0	147 ± 6 [3]	147 ± 6
allyl	59−61 [14]	76 ± 2 [33]	136 ± 3
cyclohexenyl	(60)[a]	80 ± 4 [6]	(140 ± 5)
benzyl	52 ± 6 [34]	91 ± 4 [5]	143 ± 10
pentadienyl	64−82 [10, 12, 13]	56 ± 5 [this work]	115−143

[a] No data, assumed to be same as allyl.

The value of ΔH^0_{298} gives the C−O bond dissociation energy (BDE) in the $C_5H_7O_2$ adduct. In Table 3, values of RSE and BDE for allyl, cyclohexenyl, benzyl, and pentadienyl radicals are listed. As is shown in Table 3, the BDE of the pentadienylperoxy radical, which has the largest RSE, also has the smallest BDE. The last column in Table 3 gives the sum RSE + BDE. As can be seen, this sum is approximately constant; for these resonance-stabilized radicals, the RSE is lost as the C−O single bond is formed. For pentadienyl to fit this same pattern, the RSE would need to be near the highest values that have been proposed.

$\Delta H^0_{f,298}$ for the Pentadienyl Radical. Both experimental and theoretical values of $\Delta H^0_{f,298}$ for pentadienyl radicals have been reported. Golden and Benson[35] suggested the value 221 ± 4 kJ mol^{-1} using the resonance energy in the pentadienyl radical reported by Egger and Benson.[11] This value was revised to 205 kJ mol^{-1} by McMillen and Golden.[36] Trenwith[12] reported a value 192 ± 4 kJ mol^{-1}, which was determined from the experimental activation energy for the pyrolysis of 1,3-hexadiene. Clark et al.[9] recommended a value of 208 kJ mol^{-1} after evaluating several sets of experimental data. The BAC-MP4 calculation by Melius[31] gives 190 kJ mol^{-1} for the *E*,*E* isomer and 199 kJ mol^{-1} for the *E*,*Z* isomer. On the basis of all of the above data, the value of $\Delta H^0_{f,298}$ for the pentadienyl radical is taken to be 200 ± 10 kJ mol^{-1}. The $\Delta H^0_{f,298}$ (pentadienyl) value in Table 2, 204 kJ mol^{-1}, calculated by using the group additivity value of $C^\bullet-(C_d)_2(H)$ from Dilling,[26] shows reasonable agreement, although this is about 10 kJ mol^{-1} smaller than the value calculated by using Stein's group additivity values.[24]

$\Delta H^0_{f,298}$ for the Pentadienylperoxy Radical. Because values of $\Delta H^0_{f,298}$ for the pentadienyl radical, (200 ± 10) kJ mol^{-1}, and the $\Delta H^0_{f,298}$ value for the $C_5H_7 + O_2$ reaction, (−56

± 5) kJ mol^{-1}, have been determined, the value of $\Delta H^0_{f,298}$ for the pentadienylperoxy radical can be evaluated as (144 ± 11) kJ mol^{-1}. This value is in good agreement with the group additivity value for $C_5H_7O_2$ (b) in Table 2.

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(29) For example, the difference between GAV values $C^\bullet{-}(C)(C_d)(H)$ of 29.4 J mol^{-1} K^{-1} and $C^\bullet{-}(C)_2(H)$ of 45.0 J mol^{-1} K^{-1} is 15.6 J mol^{-1} K^{-1}, and also that between $C^\bullet{-}(C_d)(H)_2$ of 115.7 J mol^{-1} K^{-1} and $C^\bullet{-}(C)(H)_2$ of 128.5 J mol^{-1} K^{-1} is 12.8 J mol^{-1} K^{-1}.

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