Thermochemistry of the R−O_2 Bond in Alkyl and Chloroalkyl Peroxy Radicals

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Earlier experimental results on the kinetics of relaxation to equilibrium in $R + O_2 \rightleftarrows RO_2$ reactions (R = CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9, CH_2Cl, $CHCl_2$, and CCl_3) are reanalyzed using an improved kinetic mechanism which accounts for further reactions of the RO_2 adduct. Reaction enthalpy $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ values are obtained from the third-law treatment of the temperature dependencies of the equilibrium constants $K_P(T)$ resulting from the reinterpretation of the original kinetic data. The R−O_2 bond strengths for alkyl and chloroalkyl radicals (R = $\cdot C(CH_3)_iCl_jH_k$, $i + j + k = 3$) can be represented by a linear function of the numbers of C−C (N_{C-C}) and C−Cl (N_{C-Cl}) bonds at the C atom forming the C−O bond: $-\Delta H°_{298}(R + O_2 \rightleftarrows RO_2) = H_{CH_3} + h_{C-C}N_{C-C} + h_{C-Cl}N_{C-Cl}$ ($H_{CH_3} = 139.9$, $h_{C-C} = 5.7$, $h_{C-Cl} = -16.1$ kJ mol^{-1}). The values of $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ are used to calculate the enthalpies of formation for the RO_2 peroxy radicals and ROOH hydroperoxides.

Introduction

The oxidation of alkyl radicals ($R + O_2$) is of key importance for understanding the mechanisms of the combustion of hydrocarbons.[1] Reactions of chlorinated alkyl radicals with O_2 play a similar role in the oxidation of chlorinated hydrocarbons. At low temperatures the main channel of the $R + O_2$ reaction is the reversible formation of a peroxy radical:

$$R + O_2 \rightleftarrows RO_2 \qquad (A)$$

At higher temperatures the equilibrium is shifted to the left and the overall reaction is dominated by further rearrangement of the excited RO_2 adduct—internal abstraction of an H atom in the β position with the formation of an $R_{-H}OOH$ intermediate which then decomposes to an olefin and HO_2 radical:

$$R + O_2 \rightleftarrows RO_2 \rightarrow R_{-H}OOH \rightarrow R_{-H} + HO_2 \qquad (B')$$

Recent ab initio results of Ignatyev et al.[2] suggest an alternative mechanism of the RO_2 rearrangement (for R = C_2H_5) proceeding without the formation of the $R_{-H}OOH$ intermediate but rather via a direct concerted olefin elimination:

$$R + O_2 \rightleftarrows RO_2 \rightarrow R_{-H} + HO_2 \qquad (B'')$$

This rearrangement (B′ or B″) can be present at low temperatures as well, but in that case it represents only a minor fraction of the overall reaction.

The knowledge of the thermodynamic parameters of the RO_2 adduct and, in particular, the enthalpy of the R−O_2 bond formation ($\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$) is central to understanding and predicting the change of the mechanism of the $R + O_2$ reactions with temperature from reversible addition (A) to rearrangement and decomposition of adduct (B). The values of $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ depend on the chemical composition of the R radical, including the nature and number of chemical groups bonded to the carbon atom forming the C−O bond.

During the past decade, a series of experimental laser photolysis/ photoionization mass spectrometry studies of relaxation to equilibria in the reactions of alkyl and chlorinated alkyl radicals with O_2 yielded temperature dependencies of the corresponding equilibrium constants ($K_P(T)$).[3−10] These K_P vs T dependencies (together with similar data obtained by other methods[8,11] where available) were used in second-law and third-law analyses to obtain the R−O_2 bond dissociation enthalpies. In all of these experiments, radicals were produced at elevated temperatures in a tubular flow reactor by excimer laser photolysis of suitable precursors, and their kinetics were monitored in real time by time-resolved photoionization mass spectrometry.

In the absence of molecular oxygen, the decay of the radicals was purely exponential and attributed to a heterogeneous wall reaction. In the presence of O_2, the kinetics of radicals displayed a more complex behavior which could be described by a double-exponential decay function. The kinetics of R radicals in such a system is affected by the following processes (described, for convenience, by corresponding first-order rate constants α, β, γ, and δ shown in parentheses):[9]

Step 1: heterogeneous wall reaction:

$$R \rightarrow \text{heterogeneous loss} \qquad (\gamma)$$

Step 2: reversible O_2 addition (α) and decomposition of adduct (β):

$$R + O_2 \rightleftarrows RO_2 \qquad (\alpha, \beta)$$

Step 3: further reaction of the RO_2 adduct (isomerization and/or heterogeneous wall reaction):

$$RO_2 \rightarrow \text{further reaction} \qquad (\delta)$$

Relaxation to equilibrium has been experimentally studied in the following reactions of alkyl and chlorinated alkyl radicals with O_2:

$$CH_3 + O_2 \rightleftarrows CH_3O_2{}^{3} \qquad (1)$$

$$C_2H_5 + O_2 \rightleftarrows C_2H_5O_2{}^{4,5} \qquad (2)$$

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$$i\text{-}C_3H_7 + O_2 \rightleftarrows i\text{-}C_3H_7O_2{}^{6} \tag{3}$$

$$t\text{-}C_4H_9 + O_2 \rightleftarrows t\text{-}C_4H_9O_2{}^{4} \tag{4}$$

$$CH_2Cl + O_2 \rightleftarrows CH_2ClO_2{}^{7} \tag{5}$$

$$CHCl_2 + O_2 \rightleftarrows CHCl_2O_2{}^{7} \tag{6}$$

$$CCl_3 + O_2 \rightleftarrows CCl_3O_2{}^{8} \tag{7}$$

$$CH_3CHCl + O_2 \rightleftarrows CH_3CHClO_2{}^{9} \tag{8}$$

$$CH_3CCl_2 + O_2 \rightleftarrows CH_3CCl_2O_2{}^{10} \tag{9}$$

$$(CH_3)_2CCl + O_2 \rightleftarrows (CH_3)_2CClO_2{}^{10} \tag{10}$$

In all but the most recent (reactions 8−10)[9,10] of these laser photolysis/ photoionization mass spectrometry studies of relaxation to equilibria in the R + O_2 reactions, the influence of the last step (3) on the double-exponential kinetics of the R radicals was neglected. These studies were recently criticized by Benson[12] for this failure to properly account for the possibility of further reaction of the RO_2 adduct.

In the current work, we reanalyze the experimental results of these earlier studies of reactions 1−7 using the mechanism described by steps 1−3 to obtain the temperature dependencies of the corresponding equilibrium constants. Enthalpy values ($\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$) for the $R + O_2 \rightleftarrows RO_2$ addition reactions are obtained in the third-law treatment. Reaction entropy values required to determine $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ are either taken from the previous studies (for most of the reactions considered) or calculated from molecular properties obtained from the experimental and ab initio results of previous (for C_2H_5, $C_2H_5O_2$, i-C_3H_7, and t-C_4H_9) and current (i-$C_3H_7O_2$ and t-$C_4H_9O_2$) investigations. The resultant $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ values are compared with the predictions of the group additivity method.

The values of $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ are affected by the substitution of functional groups (X) for H atoms on the carbon atom forming the R−O bond. Strengthening of the R−O_2 bond with the increasing complexity of the R group has been noticed for alkyl R radicals.[4,6] The effect of weakening of the R−O_2 bond for the case of X = Cl has been observed for the CH_NCl_{3-N}, $CH_3CH_NCl_{2-N}$, and $(CH_3)_2CH_NCl_{1-N}$ classes of radicals.[7−10] The data on $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ obtained in the current analysis quantitatively confirm these substitution effects. The effects of chlorine and $-CH_3$ substitution at the radical site of the R radicals can be expressed via a linear dependence of $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ on the corresponding numbers of C−C and C−Cl bonds. These results can be used to predict the $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ values for larger alkyl and chlorinated alkyl radicals within the framework of the group additivity[13] approach, i.e., under the assumption that group contribution values depend only on the nearest ligands.

Finally, the R−O_2 bond strengths obtained in the current study are used to calculate the enthalpies of formation of the corresponding peroxy radicals (RO_2) and hydroperoxides (ROOH).

Method

The kinetics of the R radical in a system of steps 1−3 can be described by the following double-exponential expression:[9]

$$[R]_t = A\exp(-\lambda_1 t) + B\exp(-\lambda_2 t) \tag{I}$$

where

$$\lambda_{1,2} = {}^1/_2(\xi \pm [\xi^2 - 4(\beta\gamma + \alpha\delta + \delta\gamma)]^{1/2}) \tag{II}$$

$$A = [R]_0\frac{\alpha + \gamma - \lambda_2}{\lambda_1 - \lambda_2} \tag{III}$$

$$B = [R]_0 - A \tag{IV}$$

$$\xi = \alpha + \beta + \gamma + \delta \tag{V}$$

These formulas can be obtained by solving a corresponding system of differential equations:

$$\begin{aligned} d[R]/dt &= -(\alpha + \gamma)[R] + \beta[RO_2] \\ d[RO_2]/dt &= \alpha[R] - (\beta + \delta)[RO_2] \end{aligned}$$

which results in the determinant equation

$$\begin{vmatrix} -\alpha - \gamma + \lambda & \beta \\ \alpha & -\beta - \delta + \lambda \end{vmatrix} = 0$$

the solution of which is given by formula II. Setting the appropriate boundary conditions ($[R]_{(t=0)} = [R]_0$, $[RO_2]_{(t=0)} = 0$, $[R]_{(t=\infty)} = [RO_2]_{(t=\infty)} = 0$), noting that

$$[RO_2]_t = C(\exp(-\lambda_1 t) - \exp(-\lambda_2 t)) \tag{I′}$$

and substituting formulas I and I′ into the above differential equations, one obtains eqs III and IV for A and B.

Equations II−V can be inverted to obtain the values of α, β, and δ from the experimentally determined values of γ, F, λ_1, and λ_2:

$$\alpha = \frac{\lambda_1 + F\lambda_2}{1 + F} - \gamma \tag{VI}$$

$$\delta = \alpha^{-1}\left[\lambda_1\lambda_2 - \gamma\frac{\lambda_1 + \lambda_2 F}{1 + F}\right] \tag{VII}$$

$$\beta = \lambda_1 + \lambda_2 - \alpha - \gamma - \delta \tag{VIII}$$

The authors of refs 3, 4, and 6−8 reported the values of λ_1, λ_2, $F = A/B$ (obtained in the equilibrium experiments), and wall rate γ (determined separately in the absence of O_2). Step 3, further reaction of the RO_2 adduct, was not taken into account in these earlier studies, which is equivalent to postulating $\delta = 0$ and resulted in incorrect values of equilibrium constants. We obtained the values of equilibrium constants $K_P = \alpha/(\beta P(O_2))$ by reinterpreting the experimental results of refs 3, 4, and 6−8 with the help of formulas VI−VIII. The conditions of the original experiments, initially reported parameters (F, λ_1, λ_2, and γ), and those obtained in the reinterpretation (α, β, δ, and equilibrium constants) are listed in Table 1 for R = CH_3, C_2H_5, i-C_3H_7, t-C_4H_9, CH_2Cl, $CHCl_2$, and CCl_3. Reaction of the RO_2 adduct, step 3, was included in the original treatment of the results of the experiments on the reactions of CH_3CHCl,[9] CH_3CCl_2,[10] and $(CH_3)_2CCl$[10] with O_2, and therefore no corrections were required in these cases.

Thermochemistry of Reactions 1−7

The enthalpies of reactions 1−7 at room temperature are obtained from the recalculated values of $K_P(T)$ (Table 1) using the third-law analysis. The procedures used were described before.[3,9] Such calculations require knowledge of the temper-

TABLE 1: Conditions, Original Results, and Results of the Reinterpretation of the Experiments on the Relaxation to Equilibrium in the R + $O_2 \rightleftarrows RO_2$ Reactions (R = CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9, CH_2Cl, $CHCl_2$, CCl_3)

									$\ln(K_P/\text{bar}^{-1})$			
T/K	$[O_2]/10^{-5}$ bar	γ/s^{-1}	λ_1/s^{-1}	λ_2/s^{-1}	F	α/s^{-1}	β/s^{-1}	δ/s^{-1}	new[a]	old[b]	K_P(new)/K_P(old)	f[c]
CH_3[3]												
694	174.3	9.1	131	6.4	4.28	98.3	24.25	5.752	7.752	7.326	1.531	0.250
713	185.4	10.0	134	4.5	2.90	90.8	35.22	2.489	7.237	7.102	1.145	0.265
731	414.4	14.2	255	13.3	3.50	187.1	53.97	13.04	6.729	6.297	1.541	0.280
732	167.2	14.2	150	17.9	1.65	86.0	47.70	20.05	6.983	6.280	2.018	0.277
752	325.3	11.0	134	12.7	1.44	73.3	48.56	13.85	6.140	5.639	1.650	0.288
755	605.9	13.9	368	22.0	2.47	254.4	96.54	25.17	6.075	5.611	1.591	0.297
755	285.7	13.9	219	21.6	1.26	117.8	81.63	27.31	6.224	5.650	1.775	0.297
772	741.7	12.4	423	16.8	1.70	260.2	147.9	19.34	5.469	5.223	1.278	0.313
772	357.7	12.4	291	19.1	0.86	132.4	138.8	26.50	5.586	5.234	1.423	0.313
791	798.4	9.3	473	16.3	1.11	247.3	210.3	22.43	4.992	4.791	1.223	0.316
811	815.7	9.3	434	17.5	0.51	148.9	260.6	32.69	4.249	4.003	1.278	0.334
C_2H_5[4]												
609	1.358	23.1	100	17.8	2.95	56.1	22.78	15.83	12.11	11.05	2.876	0.0416
617	3.080	20.7	145	16.0	4.65	101.5	23.89	14.94	11.83	10.86	2.646	0.0417
624	4.023	22.0	205	36.6	2.58	136.0	41.99	41.65	11.30	9.915	3.979	0.0417
634	4.296	22.8	180	26.5	3.40	122.3	33.83	27.56	11.34	10.15	3.292	0.0418
654	4.448	18.9	182	38.4	1.43	104.0	48.01	49.48	10.79	9.388	4.078	0.0421
654	9.514	18.9	331	56.3	2.66	237.0	63.21	68.14	10.58	9.120	4.313	0.0421
i-C_3H_7[6]												
592	1.337	29.5	392	60.8	1.91	248.7	99.49	75.12	12.14	11.01	3.079	−0.114
602	3.546	28.1	460	31.0	4.04	346.8	84.41	31.71	11.66	11.02	1.893	−0.121
612	2.867	23.6	350	15.4	4.17	261.7	66.75	13.37	11.83	11.46	1.442	−0.129
632	6.171	24.2	559	50.7	3.46	420.8	106.8	57.88	11.06	10.20	2.379	−0.145
632	4.144	24.2	774	84.5	2.66	561.4	168.2	104.7	11.30	10.33	2.633	−0.145
652	9.322	24.8	889	128	1.81	593.4	223.7	175.1	10.26	9.100	3.179	−0.163
652	4.732	24.8	735	106	0.541	302.0	298.4	215.7	9.971	8.882	2.969	−0.163
672	9.180	13.2	1150	173	0.696	560.7	411.9	337.2	9.604	8.408	3.310	−0.181
672	7.650	13.2	848	147	0.393	331.6	300.2	350.1	9.578	8.032	4.689	−0.181
692	23.30	8.2	1110	189	1.12	667.4	316.7	306.7	9.110	7.753	3.882	−0.198
t-C_4H_9[4]												
550	0.3729	46.8	185	37.3	3.51	105.5	35.70	34.35	13.58	12.23	3.850	−0.265
560	0.4023	45.6	166	39.0	3.70	93.4	28.93	37.09	13.60	11.95	5.208	−0.284
560	0.8278	45.6	276	48.7	4.00	184.9	44.70	49.46	13.12	11.63	4.438	−0.284
560	0.8278	41.4	346	49.7	3.71	241.7	60.75	51.86	13.08	11.85	3.437	−0.284
570	0.8369	45.9	345	63.6	2.27	213.0	78.91	70.75	12.68	11.40	3.596	−0.303
570	1.621	45.9	505	65.4	4.20	374.6	80.14	69.80	12.57	11.32	3.503	−0.303
580	1.662	40.9	342	73.7	2.96	233.3	58.23	83.22	12.39	10.62	5.902	−0.321
CH_2Cl[7]												
562	2.047	11.1	299	41.4	5.15	246.0	36.73	46.56	8.360	8.293	1.069	0.159
572	2.503	8.6	311	46.8	4.00	249.6	44.75	54.89	7.958	7.945	1.013	0.165
582	3.445	11.9	335	36.2	4.78	271.4	47.07	40.83	7.655	7.410	1.278	0.171
582	3.445	11.7	286	53.0	3.77	225.5	39.90	61.95	7.634	7.609	1.026	0.171
592	4.083	8.8	424	54.7	2.61	312.9	87.29	69.71	6.992	6.863	1.138	0.177
592	4.874	6.8	504	54.4	2.80	378.9	103.5	69.26	6.837	6.820	1.017	0.177
592	3.344	11.4	316	41.9	2.55	227.4	66.85	52.26	7.140	7.012	1.136	0.177
602	3.891	15.6	326	43.5	2.39	227.1	73.09	53.74	6.881	6.851	1.031	0.183
612	5.735	12.1	439	36.1	2.57	314.0	104.2	44.72	6.446	6.367	1.082	0.188
612	5.735	12.1	436	53.9	1.46	268.6	131.2	78.07	6.060	5.958	1.107	0.188
612	4.094	5.6	379	30.9	2.73	280.1	84.89	39.33	6.874	6.778	1.100	0.188
612	4.094	5.6	379	19.1	3.27	289.1	80.35	23.04	6.96	6.880	1.083	0.188
633	4.094	8.8	339	18.1	1.76	213.9	111.2	23.15	6.300	6.297	1.004	0.200
633	6.708	4.9	492	30.4	1.90	327.9	146.8	42.78	5.956	5.940	1.016	0.200
633	4.985	10.7	380	30.0	1.77	242.9	116.3	40.04	6.186	6.105	1.084	0.200
644	8.369	7.9	328	30.4	1.56	203.9	103.4	43.23	5.592	5.520	1.075	0.206
654	9.565	5.8	356	38.6	1.08	197.6	127.3	63.93	5.205	5.134	1.073	0.211
664	9.514	11.5	259	26.7	1.14	138.9	96.68	38.57	5.118	4.970	1.159	0.216
$CHCl_2$[7]												
498	1.125	5.6	217	9.6	1.85	138.6	70.67	11.70	7.852	7.548	1.354	0.008
498	2.290	3.5	263	9.0	3.25	199.7	58.12	10.65	7.701	7.365	1.401	0.008
509	3.607	8.1	277	10.4	3.57	210.6	57.70	11.04	7.285	6.935	1.420	0.007
509	3.982	2.9	455	14.8	3.23	348.0	100.5	18.36	7.134	6.799	1.398	0.007
509	3.425	4.3	379	13.4	2.83	279.2	92.35	16.51	7.149	6.820	1.390	0.007
509	3.425	4.3	487	13.9	3.07	366.5	113.2	16.95	7.217	6.940	1.320	0.007
509	2.320	4.3	323	9.1	2.33	224.4	92.25	11.12	7.321	7.095	1.254	0.007
521	4.864	2.7	576	14.1	2.48	411.8	157.0	18.57	6.633	6.412	1.248	0.006
521	4.641	2.7	317	3.2	2.83	232.4	81.76	3.38	6.760	6.679	1.085	0.006
521	4.651	5.2	339	15.6	2.38	238.1	91.50	19.78	6.67	6.278	1.479	0.006
532	5.451	4.5	399	13.9	1.95	264.0	125.9	18.55	6.274	6.001	1.315	0.005

TABLE 1: (Continued)

									$\ln(K_P/\mathrm{bar}^{-1})$			
T/K	$[O_2]/10^{-5}$ bar	γ/s^{-1}	λ_1/s^{-1}	λ_2/s^{-1}	F	α/s^{-1}	β/s^{-1}	δ/s^{-1}	new[a]	old[b]	K_P(new)/K_P(old)	f[c]
						$CHCl_2$[7]						
532	7.873	10.1	572	19.8	1.72	358.9	197.5	25.29	5.763	5.520	1.275	0.005
532	4.580	10.1	488	11.2	1.68	300.0	177.3	11.85	6.234	6.105	1.138	0.005
542	5.624	1.7	435	10.0	1.50	263.3	164.6	15.36	5.953	5.774	1.197	0.004
542	4.367	3.3	469	6.7	1.08	243.4	219.2	9.80	5.842	5.752	1.094	0.004
552	5.867	1.9	637	11.9	0.94	312.9	311.9	22.20	5.426	5.290	1.146	0.002
562	5.725	4.6	391	9.4	0.69	160.6	219.1	16.15	5.119	4.970	1.161	−0.001
						CCl_3[8]						
388	1.236	2.2	210	4.1	2.55	149.8	57.26	4.84	8.295	8.134	1.175	−0.012
388	2.026	2.9	360	2.9	4.77	295.2	61.89	2.90	8.401	8.313	1.092	−0.012
388	1.459	2.7	316	16.2	5.32	265.9	45.03	18.61	8.943	8.247	2.005	−0.012
388	1.834	6.6	322	11.8	4.64	260.4	53.90	12.90	8.514	8.097	1.517	−0.012
388	1.834	6.6	343	5.6	4.45	274.5	62.13	5.37	8.424	8.270	1.167	−0.012
398	3.323	9.9	323	11.0	5.71	266.6	46.31	11.19	8.069	7.638	1.538	−0.015
398	1.733	0.7	347	11.8	2.12	238.9	102.4	16.79	7.817	7.517	1.350	−0.015
408	4.468	9.1	390	14.9	3.77	302.3	77.13	16.41	7.364	6.977	1.472	−0.018
408	4.499	5.7	386	11.3	3.67	300.1	78.74	12.80	7.329	7.029	1.350	−0.018
408	4.499	5.7	369	11.3	3.41	282.2	79.50	12.91	7.258	6.956	1.353	−0.018
418	4.509	5.9	507	15.5	2.23	348.9	148.0	19.69	6.822	6.574	1.281	−0.021
418	3.516	9.5	530	22.8	1.67	330.5	182.3	30.44	6.808	6.500	1.361	−0.021
428	3.962	3.8	392	14.2	1.10	208.3	170.9	23.18	6.268	6.018	1.285	−0.024
428	5.198	5.5	411	12.0	1.37	237.1	163.7	16.61	6.169	5.973	1.216	−0.024
439	4.104	10.8	369	20.6	0.71	154.5	190.8	33.53	5.798	5.472	1.386	−0.028

[a] Values of K_P/bar^{-1} obtained in the reinterpretation of the experimental results via formulas I−VIII. [b] Values of K_P/bar^{-1} as reported by the authors of the original studies. [c] Values of the "correction" function (see text).

ature dependencies of the thermodynamic functions (entropy and enthalpy) of the reactants (R and O_2) and products (RO_2) of the addition steps in reactions 1−7. These thermodynamic functions can be calculated from the models of R and RO_2 radicals. Such models have been used before by the authors of the original studies on reactions 1−3 and 5−7.

In the current study, we use the thermodynamic properties of R and RO_2 radicals employed in the original works for reactions 1 and 5−7. These models of reactions 5−7 were based on ab initio calculations, and that of reaction 1 on extensive experimental and ab initio data on the properties of the CH_3 and CH_3O_2 radical. The models of C_2H_5 and $C_2H_5O_2$ radicals (reaction 2) employed in the current study (Table 2) are based on the experimental vibrational frequencies of Chettur and Snelson[14] and the ab initio study of Quelch et al.[15] The properties of the i-C_3H_7 and t-C_4H_9 radicals (reactions 3 and 4) are taken from the experimental and ab initio results of Pacansky et al. (i-C_3H_7 and t-C_4H_9)[16,17] and Chen et al. (i-C_3H_7).[18] Since experimental data on the vibrational frequencies and geometry of i-$C_3H_7O_2$, and t-$C_4H_9O_2$ are unavailable, thermodynamic properties of these radicals are obtained using the results of ab initio calculations conducted in the current study.

Molecular Parameters of i-$C_3H_7O_2$, and t-$C_4H_9O_2$. We studied the geometries and harmonic vibrational frequencies of i-$C_3H_7O_2$ and t-$C_4H_9O_2$ using the ab initio unrestricted HF method with 6-31G** and 6-31G* basis sets. Internal rotations (−CH_3 torsions and rotation about the C−O bond) were studied by the UMP2 method. Geometrical structures corresponding to minima and maxima of the rotational potential energy surfaces were obtained with the full optimization at the UHF level and energy was calculated at the UMP2 level. 6-31G** and 6-31G* basis sets were used for i-$C_3H_7O_2$ and t-$C_4H_9O_2$ radicals, respectively. Structures, vibrational frequencies, and energies of these species are listed in Tables 1S−4S. The GAUSSIAN 92 system of programs[20] was used in all ab initio calculations.

One uncertain aspect of the properties of these radicals pertinent to the calculation of their entropy is the treatment of the hindered internal rotations (−CH_3 torsions and rotation about the C−O bond). In both radicals, −CH_3 torsions (periodic triple well) were approximated by a symmetrical ($\sigma = 3$) sinusoidal potential. Barrier heights for these degrees of freedom obtained at UHF and UMP2 levels agree within 1 kJ mol^{-1} (UMP2-level values corrected for the zero-point vibrational energy were used in the models). The potential energy surface of the C−OO torsional motion in t-$C_4H_9O_2$ has a symmetry factor of 3 and is also approximated by a sinusoidal potential. The C−OO torsion in i-$C_3H_7O_2$ has a potential of a more complex shape consisting of three minima and three maxima. Two of the three maxima (corresponding to O−O bond eclipsed with C−C bonds) are identical in height and equal to 9.38 kJ mol^{-1} (UMP2/6-31G** level + ZPVE). The third maximum is significantly lower: 2.75 kJ mol^{-1}. Of the three minima, two (corresponding to a nonsymmetric configuration with O−O bond positioned between the C−H and C−C bonds) are equal and have UMP2-level energy 1.17 kJ mol^{-1} below that of the third minimum, a symmetric configuration with O−O bond positioned between the two C−C bonds. However, the energy difference between the symmetric and nonsymmetric conformations noticeably reduces with the improvement of the level of calculations (from 2.96 kJ mol^{-1} at the UHF level to 1.17 kJ mol^{-1} at the MP2 level). It is possible that with further improvement of the level of ab initio theory this trend will continue, and the energy of nonsymmetric conformation will be equal to or higher than that of the symmetric conformation. Considering this, and the already small energy difference obtained at the MP2 level, we use the symmetric conformation (O−O bond positioned between the two C−C bonds) as the reference state for computing the torsional barriers and as a basis for the model of the i-$C_3H_7O_2$ radical. In the model of the i-$C_3H_7O_2$ radical, C−OO torsion was treated as nonsymmetrical hindered rotations with symmetrical sinusoidal potential (triple well) with the barrier heights taken as an average of three maxima calculated at the UMP2/6-31G** level with corrections for the zero-point vibrational energy (scaled[19] by a factor of 0.91). An alternative treatment is to neglect the lowest barrier compared to the other two much higher barriers and treat the C−OO torsion as a double-well

TABLE 2: Properties of the C_2H_5, $C_2H_5O_2$, *i*-C_3H_7, *i*-$C_3H_7O_2$, *t*-C_4H_9, and *t*-$C_4H_9O_2$ Radicals Used in Thermodynamic Calculations

	Vibrational Frequencies (cm^{-1})	
C_2H_5:[a]	3114, 3036, 2987, 2920, 2844, 1442, 1442, 1383, 1369, 1133, 1185, 1025, 783, 532	
$C_2H_5O_2$:[b]	3016, 2983, 2977, 2938, 2911, 1474, 1451, 1389, 1351, 1380, 1242, 1112, 1163, 1136, 1009, 838, 800, 499, 306	
i-C_3H_7:[c]	3069, 2920, 2925, 2830, 1468, 1468, 1378, 1126, 995, 855, 369, 340, 2920, 2926, 2830, 1468, 1468, 1388, 1301, 1107, 892, 890	
i-$C_3H_7O_2$:[d]	287, 358, 396, 597, 762, 902, 909, 917, 1077, 1107, 1149, 1172, 1323, 1345, 1379, 1388, 1433, 1441, 1444, 1460, 2843, 2847, 2886, 2905, 2910, 2918, 2925	
t-C_4H_9:[e]	3187, 3136, 3038, 1562, 1539, 1462, 1351, 1050, 974, 388, 3137, 3043, 1557, 1485, 1157, 793, 282, 3183, 1540, 1001	
t-$C_4H_9O_2$:[d]	262, 323, 347, 389, 434, 538, 716, 862, 898, 904, 942, 1022, 1030, 1136, 1206, 1235, 1263, 1388, 1389, 1410, 1441, 1453, 1453, 1464, 1464, 1483, 2862, 2862, 2870, 2919, 2921, 2930, 2930, 2936, 2940	
	Rotational Constants (cm^{-1}), Symmetry Numbers, and Rotational Barriers (kJ mol^{-1})	
	Overall Rotations	
C_2H_5:	$B = 1.2256$;	$\sigma = 1$
$C_2H_5O_2$:	$B = 0.2889$;	$\sigma = 1$
i-C_3H_7:	$B = 0.4404$;	$\sigma = 2$
i-$C_3H_7O_2$:	$B = 0.1604$;	$\sigma = 1$
t-C_4H_9:	$B = 0.2191$;	$\sigma = 3$
t-$C_4H_9O_2$:	$B = 0.1132$;	$\sigma = 1$
	Internal Rotations	
C_2H_5:	$a_1(CH_3{-}CH_2) = 15.187$;	$\sigma = 6$; $V_0 = 0$
$C_2H_5O_2$:	$a_1(CH_3{-}CH_2O_2) = 6.130$;	$\sigma = 3$; $V_0 = 11.3$
	$a_2(CH_3CH_2{-}O_2) = 2.183$;	$\sigma = 1$; $V_0 = 6.0^f$
i-C_3H_7:	$a_{1,2}(CH_3{-}C(CH_3)H) = 6.676$;	$\sigma = 3$; $V_0 = 3.05$
i-$C_3H_7O_2$:	$a_{1,2}(CH_3{-}C(CH_3)HO_2) = 5.561$;	$\sigma = 3$; $V_0 = 15.5$
	$a_3((CH_3)_2CH{-}O_2) = 1.537$;	$\sigma = 1$; $V_0 = 7.17^f$
t-C_4H_9:	$a_{1,2,3}(CH_3{-}C(CH_3)_2) = 5.629$;	$\sigma = 3$; $V_0 = 6.38$
t-$C_4H_9O_2$:	$a_{1,2,3}(CH_3{-}C(CH_3)_2O_2) = 5.509$;	$\sigma = 3$; $V_0 = 16.03^g$
	$a_4((CH_3)_3C{-}O_2) = 1.491$;	$\sigma = 3$; $V_0 = 10.07$

Entropies Calculated Using the Above Models

$S°_{298}(C_2H_5) = 247.2$ J mol^{-1} K^{-1}	$S°_{298}(C_2H_5O_2) = 311.8$ J mol^{-1} K^{-1}
$S°_{298}(i\text{-}C_3H_7) = 289.4$ J mol^{-1} K^{-1}	$S°_{298}(i\text{-}C_3H_7O_2) = 338.7$ J mol^{-1} K^{-1}
$S°_{298}(t\text{-}C_4H_9) = 314.0$ J mol^{-1} K^{-1}	$S°_{298}(t\text{-}C_4H_9O_2) = 353.9$ J mol^{-1} K^{-1}

[a] Properties of C_2H_5 are a combination of experimental data of Chettur and Snelson[14] and ab initio results of Quelch et al.[15] [b] Properties of $C_2H_5O_2$ are obtained from the ab initio study of Quelch et al.[15] [c] Properties of *i*-C_3H_7 are taken from the experimental and ab initio results of Pacansky et al.[16,17] and Chen et al.[18] [d] Properties of *i*-$C_3H_7O_2$ and *t*-$C_4H_9O_2$ from ab initio calculations conducted in the current study (see text). Vibrational frequencies are scaled[19] by a factor of 0.89. [e] Properties of *t*-C_4H_9 are taken from the ab initio study of Pacansky et al.[17] [f] Average of three nonequal maxima on the rotational potential energy surface. An alternative approach is to neglect the lower-energy maxima (see text). [g] Average of the barriers for two $-CH_3$ groups in the gauche position and one in the anti position relative to the O$-$O bond.

sinusoidal potential. Such an alternative model results in a value of the *i*-$C_3H_7O_2$ room-temperature entropy which is lower by 1.36 J mol^{-1} K^{-1}. This difference in entropy is taken into account in assessing the uncertainty of the $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ value obtained in the third-law treatment. A similar approach to the treatment of the R$-O_2$ internal rotor was used for R = C_2H_5. Reduced moments of inertia for internal rotations were calculated from the structural data by the method of Pitzer and Gwinn.[21,22] Thermodynamic functions of the hindered internal rotations were obtained from interpolation of the tables of Pitzer and Gwinn.[21] Vibrational frequencies obtained in ab initio calculations were scaled by a factor of 0.89.[19] Properties of the C_2H_5, $C_2H_5O_2$, *i*-C_3H_7, *i*-$C_3H_7O_2$, *t*-C_4H_9, and *t*-$C_4H_9O_2$ radicals used in thermodynamic calculations are listed in Table 2.

Determination of $\Delta H°_{298}$ of the $R + O_2 \rightleftarrows RO_2$ Reactions. The room-temperature enthalpies of reactions 1$-$7 were obtained from the data on $K_P(T)$ using a third-law analysis. First, the values of $\Delta G°_T$ of reactions 1$-$7 were obtained directly from the values of the equilibrium constant:

$$\ln(K_p/\text{bar}^{-1}) = -\Delta G°_T/RT \qquad \text{(IX)}$$

where K_P is the equilibrium constant in bar^{-1}.

The addition of a small "correction"

$$f(T) = \frac{\Delta H°_T - \Delta H°_{298}}{RT} - \frac{\Delta S°_T - \Delta S°_{298}}{R}$$

converts the right-hand side of the eq IX to a linear function of $1/T$ with the intercept at $1/T = 0$ equal to $\Delta S°_{298}/R$ and slope of the function equal to $-\Delta H°_{298}/R$:

$$\ln(K_p) + f(T) = \frac{\Delta S°_{298}}{R} - \frac{\Delta H°_{298}}{RT}$$

The values of this "correction" function, $f(T)$, ($\leq$6% of $\ln(K_P)$) and $\Delta S°_{298}$ of reactions 1$-$7 were either taken from the original publications (reactions 1 and 5$-$7) or calculated using the new models of R and RO_2 radicals described above (reactions 2$-$4, Table 2). The resultant values of $f(T)$ are listed in Table 1. The values of $\Delta H°_{298}$ were obtained from the slopes of the lines drawn through the experimental values of ($\ln(K_P) + f(T)$) and the calculated intercepts $\Delta S°_{298}/R$ (Figures 1$-$3). In addition to the K_P vs T data of Table 1, data of similar type reported by Khachatryan et al. (reaction 1) and Russell et al. (reaction 7, results of UV absorption experiments that do not require reinterpretation) were used. The values of $\Delta S°_{298}$ used and the resultant values of $\Delta H°_{298}$ of reactions 1$-$7 are listed in Table 3.

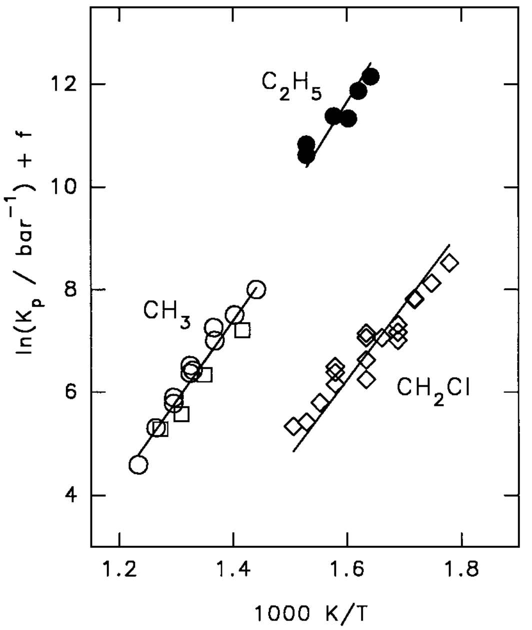

Figure 1. Modified van't Hoff plot of (ln(K_P) + $f(T)$) vs 1000 K/T for R + O_2 $\rightleftarrows$ RO_2 reactions. Symbols represent reinterpreted experimental data. Reaction 1 (R = CH_3): open circles, Slagle and Gutman;[3] open squares, Khachatryan et al. (data as reported by the authors).[11] Reaction 2 (R = C_2H_5): filled circles, Slagle et al.[4] Reaction 5 (R = CH_2Cl): open diamonds, Russell et al.[7] Lines represent the results of the third-law fits (see text).

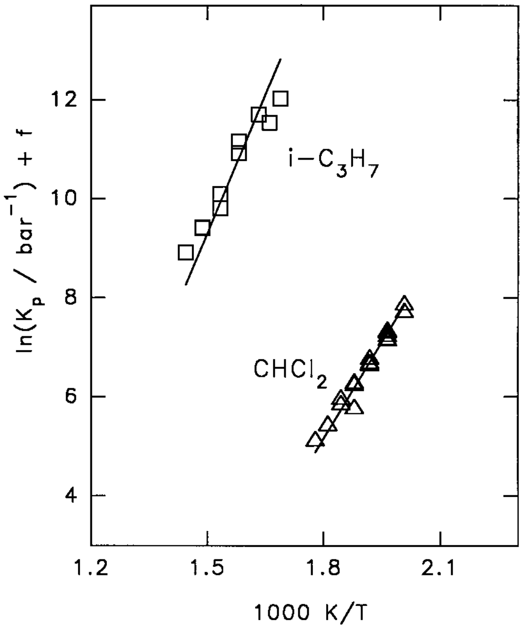

Figure 2. Modified van't Hoff plot of (ln(K_P) + $f(T)$) vs 1000 K/T for R + O_2 $\rightleftarrows$ RO_2 reactions. Symbols represent reinterpreted experimental data. Reaction 3 (R = i-C_3H_7): squares, Slagle and Gutman.[6] Reaction 6 (R = $CHCl_2$): triangles, Russell et al.[7] Lines represent the results of the third-law fits (see text).

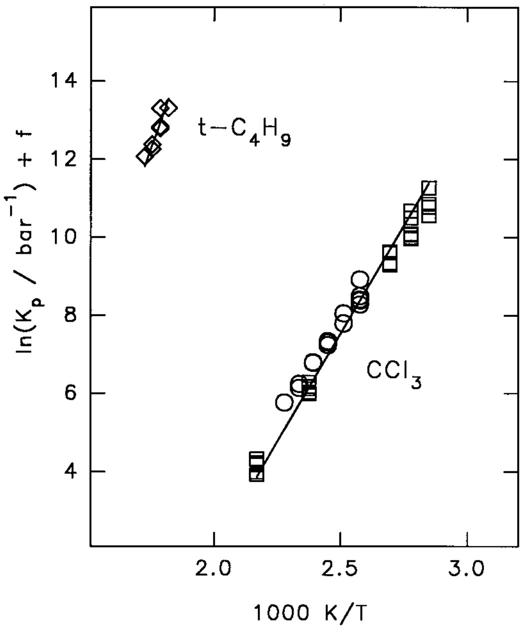

Figure 3. Modified van't Hoff plot of (ln(K_P) + f(T)) vs 1000 K/T for R + O_2 $\rightleftarrows$ RO_2 reactions. Symbols represent reinterpreted experimental data. Reaction 4 (R = t-C_4H_9): diamonds, Slagle et al.[4] Reaction 7 (R = CCl_3), Russell et al.:[8] circles, results obtained in photoionization mass spectrometry experiments; squares, results obtained using UV absorption spectroscopy (data as reported by the authors). Lines represent the results of the third-law fits (see text).

Discussion

Values of $\Delta H°_{298}$(R + O_2 $\rightleftarrows$ RO_2) and Kinetic Parameters of Reactions 1−7. As can be seen from the data in Tables 1 and 3, reinterpretation of the experimental data on the kinetics of relaxation to equilibrium in reactions 1−7 within the framework of the model of steps 1−3 (formulas I−VIII) results in a change of the values of $K_P(T)$ and $\Delta H°_{298}$(R + O_2 $\rightleftarrows$ RO_2) compared to those originally reported. These changes due to corrected treatment range from negligible (R = CH_2Cl) to significant (R = C_2H_5, i-C_3H_7, t-C_4H_9). Some contribution to the changes in $\Delta H°_{298}$(R + O_2 $\rightleftarrows$ RO_2) is due to the fact that in some of the original studies on the determination of $K_P(T)$ third-law values of enthalpy were obtained from a slope of a straight line fitted through the ln(K_P) vs $1/T$ data with $\Delta S°_{298}/R$ at $1/T = 0$ treated as an additional data point, while in the current treatment the line is forced through the $\Delta S°_{298}/R$ at $1/T = 0$ point obtained from the calculated entropy. Formulas VI−VIII also provide for the determination of α, β, and δ: the first-order rates of the R + O_2 addition (α = $k_{ADD}[O_2]$), reverse decomposition of the RO_2 adduct (β), and the decay of the RO_2 adduct due to other reactions (δ, Table 1). One should note, however, that the conditions of the original experiments (refs 3, 4, and 6−8) were selected to optimize only the determination of the equilibrium constants. This results in expected high uncertainties of the α, β, and δ kinetic parameters listed in Table 1, the uncertainties that, in addition, are not easily estimated. The values of α and β are expected to be in the falloff region which will complicate any potential use of these data. The α and β temperature dependencies exhibit an anticipated qualitative behavior: β values steeply increase with temperature (as expected for a rate constant of a decomposition reaction), and the values of α/$[O_2]$ (corresponding to the second-order addition rate constant) somewhat decrease with temperature, as is expected for a barrierless addition in the falloff. The rate constant of the decay of the adduct, δ, as mentioned above, is a sum of the rate constant of RO_2 heterogeneous loss and that of its further reaction to products other than R + O_2. The fitted values of δ lie within the range 2.5−350 s^{-1}. Unfortunately, the potentially useful information on the RO_2 reaction to products cannot be separated from the rates of the wall reaction. One can note, however, that although the values of δ are considerably lower than those of β for R = CH_3, $CHCl_2$, and CCl_3 (i.e., further reaction of RO_2 is minor compared to the reverse decomposition to R + O_2), for R = C_2H_5, i-C_3H_7, and t-C_4H_9 δ and β become comparable and δ exhibits a trend to

TABLE 3: Thermodynamic Functions of the R + $O_2 \rightleftarrows RO_2$ Reactions Obtained in the Current and Previous Studies (kJ mol^{-1} and J mol^{-1} K^{-1})

R	$-\Delta H°_{298}$ (old)^{a}	$-\Delta S°_{298}$	$-\Delta H°_{298}$ (new)^{b}	$-\Delta H°_{298}$ (GA)^{c}	exp data (ref)
CH_3	135.6 ± 2.9	129.9 ± 1.5^{d}	137.0 ± 3.8^{e}	138.2 (±1.0)	3
C_2H_5	142.7 ± 2.1	140.5 ± 5.4^{f}	148.4 ± 8.4^{e}	145.8	4
i-C_3H_7	157.7 ± 7.5	155.9 ± 6.7^{f}	155.4 ± 9.6^{e}	150.3	6
t-C_4H_9	153.6 ± 7.9	165.3 ± 6.0^{f}	152.8 ± 7.4^{e}	154.1	4
CH_2Cl	121.0 ± 11.0	144.0 ± 11.0^{d}	122.4 ± 10.5^{e}	117.4 (±3.1)	7
$CHCl_2$	106.0 ± 6.0	152.0 ± 12.0^{d}	108.2 ± 8.2^{e}	102.5 (±3.0)	7
CCl_3	83.3 ± 4.2	167.4 ± 12.6^{d}	92.0 ± 6.4^{e}	g	8
CH_3CHCl		152.3 ± 3.3^{h}	131.2 ± 1.8^{h}	143.6	9
CH_3CCl_2		159.6 ± 4.0^{h}	112.2 ± 2.2^{h}	127.4	10
$(CH_3)_2CCl$		165.5 ± 6.0^{h}	136.0 ± 3.8^{h}	g	10

[a] Values of $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ reported in the original studies where step 3 (further reaction of the RO_2 adduct) was neglected in the interpretation of the experimental data. [b] Values of $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ obtained in the current study via reinterpretation of the original experimental data. [c] Values of $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ estimated by the group additivity method[13] with newer values of group contributions (see text). $\Delta H_f°_{298}$ group values for chlorinated alkyl groups (kJ mol^{-1}) are taken from Ritter and Bozzelli[23a] (C−C/Cl_2/O: −78.2; C−C/Cl/H/O: −72.0) and Dilling[24] (•C−C/Cl_2: 99.2; •C−C/Cl/H: 121.3). Experimental values of $\Delta H_f°_{298}$(R) were used for R = CH_3,[25] CH_2Cl,[26] and $CHCl_2$.[26] Uncertainties in parentheses are due to the experimental error limits in $\Delta H_f°_{298}$(R). [d] Calculated reaction entropy values taken from the corresponding original studies. [e] Error limits are a combination of factors resulting from statistical uncertainty of the fit (2σ), uncertainty in entropy, and experimental (originally reported) error limits of equilibrium constants (up to a factor of 2 in most of the reanalyzed studies). [f] Error limits in entropy are due to the uncertainties in the low-frequency vibrations (primarily pyramidal bends) and in the treatment of the R−O_2 hindered internal rotor (see text). [g] Group values are unavailable. [h] No reinterpretation of experimental data was requires since mechanism of steps 1−3 was applied to data analysis in the original studies.

growth with temperature. This can be explained by the isomerization of RO_2 becoming important at the temperatures of experiments, as suggested by Benson.[12] In the special case of R = CH_2Cl, δ and β are comparable but δ does not display any noticeable temperature dependence, which can be explained by a high rate of CH_2ClO_2 wall decay. The values of δ for R = C_2H_5 (ranging from 15 to 68 s^{-1}) agree, in order of magnitude, with the isomerization rates predicted by Wagner et al.[5] based on their theoretical analysis of the experimental data on $C_2H_5 + O_2$ system (increasing from 8 s^{-1} at 610 K to 26 s^{-1} at 650 K). Similarly, the δ values for R = i-C_3H_7 (13−350 s^{-1}) are close, within order-of-magnitude accuracy, to the estimates by Benson[12] (500−20000 s^{-1}).

Cl and −CH_3 Substitution Effects. The general tendency of the strengthening of the R−O_2 bond with increasing complexity of the R alkyl group has been noticed before.[4,6] An analogous (although opposite in direction) and stronger trend of the weakening of the R−O_2 bond with the substitution of chlorine for hydrogen atoms on the carbon atom forming the C−O bond has been reported by the authors of the original studies[7,8] of equilibria in reactions 5−7 and confirmed[9,10] by the experimental values of $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ for reactions 8−10. The results of the current study confirm both effects of the strengthening of the R−O_2 bond due to −CH_3 groups and the weakening due to −Cl groups bonded to the carbon atom forming the C−O bond. The data on the $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ (Table 3) cover all possible combinations of −H, −Cl, and −CH_3 groups as ligands bonded to the C atom of the C−O bond. These substitution effects can be represented in a linear form as a sum of contributions from individual C−Cl and C−C bonds (relative to the CH_3 radical):

$$-\Delta H°_{298}(R + O_2 \rightleftarrows RO_2) = H_{CH_3} + h_{C-C}N_{C-C} + h_{C-Cl}N_{C-Cl} \quad (X)$$

where H_{CH_3} corresponds to the case of no C−C and C−Cl bonds (i.e., R = CH_3), N_{C-C} and N_{C-Cl} are the numbers of C−C and C−Cl bonds substituted for the original C−H bonds, and h_{C-C} and h_{C-Cl} are the corresponding bond contributions. The fitted values of H_{CH_3}, h_{C-C}, and h_{C-Cl} are (error limits represent the uncertainties of the fit, 1σ):

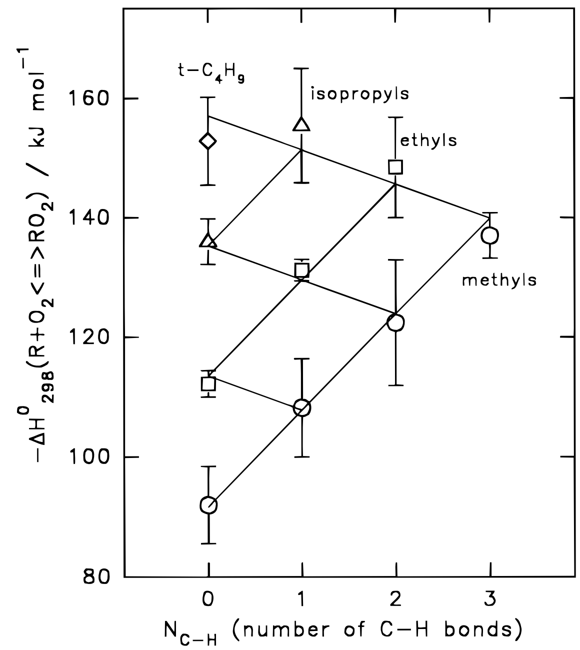

Figure 4. Dependence of $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ on the numbers of C−H (N_{C-H}), C−C (N_{C-C}), and C−Cl (N_{C-Cl}) bonds at the R radical center ($N_{C-H} + N_{C-C} + N_{C-Cl} = 3$). Symbols represent the reinterpreted experimental data (Table 3). Circles: methyl radicals, CH_iCl_{3-i} (N_{C-C} = 0, N_{C-H} = 0−3); squares: ethyl radicals, $CH_3CH_iCl_{2-i}$ (N_{C-C} = 1, N_{C-H} = 0−2); triangles: isopropyl radicals, $(CH_3)_2CH_iCl_{1-i}$ (N_{C-C} = 2, N_{C-H} = 0−1); diamond: *tert*-butyl radical, t-C_4H_9 (N_{C-C} = 3, N_{C-H} = N_{C-Cl} = 0). Lines: representation of the $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ vs N_{C-H}, N_{C-C}, and N_{C-Cl} dependence by formula X (see text). The $\Delta H°_{298}$-$(R + O_2 \rightleftarrows RO_2)$ vs N_{C-H} mode of presentation is chosen to avoid overlapping of the error limits.

$$H_{CH_3} = 139.9 \pm 2.0 \text{ kJ mol}^{-1}$$

$$h_{C-C} = 5.7 \pm 1.1 \text{ kJ mol}^{-1} \quad (XI)$$

$$h_{C-Cl} = -16.1 \pm 1.1 \text{ kJ mol}^{-1}$$

The experimental data on the R + $O_2 \rightleftarrows RO_2$ reaction enthalpy, together with their representation by formula X, are

TABLE 4: Enthalpies of Formation of RO_2 and ROOH Derived in the Current Study (kJ mol^{-1})

R	$\Delta H_f°_{298}(R)$	$\Delta H_f°_{298}(RO_2)$	$\Delta H_f°_{298}(ROOH)$	
			calculated	experimental
CH_3	146.0 ± 1.3[29,30]	9.0 ± 5.1	-139.0 ± 8.1	
C_2H_5	121.0 ± 1.5[29−31]	-27.4 ± 9.9	-175.4 ± 12.9	-173.6 ± 6.3[a]
i-C_3H_7	90.0 ± 1.7[29−31]	-65.4 ± 11.3	-213.4 ± 14.3	
t-C_4H_9	51.3 ± 1.8[29−31]	-101.5 ± 9.2	-249.5 ± 12.2	-246.0 ± 5.0[32]
CH_2Cl	117.3 ± 3.1[26]	-5.1 ± 13.6	-153.1 ± 16.6	
$CHCl_2$	89.0 ± 3.0[26]	-19.2 ± 11.2	-167.2 ± 14.2	
CCl_3	71.1 ± 2.5[33]	-20.9 ± 8.9	-168.9 ± 11.9	
CH_3CHCl	76.5 ± 1.6[26]	-54.7 ± 3.4[9]	-202.7 ± 6.4	-213.0 ± 14.2[a]
CH_3CCl_2	48.4 ± 7.6[b]	-63.8 ± 9.8[10]	-211.8 ± 12.8	-231.4 ± 9.2[a]
$(CH_3)_2CCl$				

[a] Calculated (Lay et al.[34]) by ab initio methods using isodesmic reactions. [b] Average of the two values obtained by Seetula[26] in the third-law and second-law treatments of data on the $CH_3CCl_2 + HBr \rightleftarrows CH_3CHCl_2 + Br$ reaction (see discussion in ref 10).

shown in Figure 4. The values of $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ are plotted vs the number of C−H bonds at the radical center of R, N_{C-H} ($N_{C-H} = 3 - N_{C-C} - N_{C-Cl}$). This mode of presentation is chosen to avoid overlapping of the error limits which occurs if the same data are plotted vs N_{C-C} or N_{C-Cl}.

Formula X can be used as a predictive tool for estimating the $R-O_2$ bond strength ($-\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$) for larger radicals with alkyl or chloroalkyl group bonded to O_2. In the current set of data (Table 3, Figure 4) all contributions from C−C bonds are represented by CH_3 groups attached to a carbon atom. The results, however, can be generalized in the spirit of the group additivity[13] method which assumes that the contribution of each group to the thermodynamic properties of a molecule depends only on the "central" group-forming atom and its ligands (i.e., it is independent of chemical structure beyond these ligands). Thus, formula X with parameters XI can be used for larger radicals with N_{C-C} understood as the number of C−C bonds between the C atom bonded to O_2 and other C atoms in the sp^3 configuration.

Comparison with the Predictions by the Group Additivity Method. $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ values obtained in the current study are compared with the predictions of the group additivity method in Table 3. The group additivity method (GA)[13] has proven to be a useful tool for estimating thermodynamic properties of molecules and radicals for which no experimental data are available. Since the publication of the original group contribution values by Benson[13] (based on the experimental data and best estimates available at that time), group values for new groups have been published and many older values updated using new experimental information (refs 23, 24, 27, 28, and references therein). The GA-estimated values of $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ for hydrocarbon radicals (R = CH_3, C_2H_5, i-C_3H_7, and t-C_4H_9) in Table 3 are based on the recommendations of Stocker and Pilling,[28] who analyzed new experimental and ab initio data on the thermodynamic properties of hydrocarbons and hydrocarbon radicals to derive new group contribution values.

As can be seen from Table 3, for alkyl R radicals the GA-based estimates agree with the experimental results within the uncertainty limits. This is not surprising for R = CH_3, C_2H_5, and i-C_3H_7 since Stocker and Pilling derived the enthalpy group value for the (O−C/O•) group, in part, from the values of $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ for these radicals obtained in the current study from the reanalyzed data of refs 3−5. The agreement obtained in the case of R = t-C_4H_9, however, is not inherent to the group contributions used and serves as an evidence of the accuracy of these group values.

The agreement between the experimental and GA-estimated values is not as good in the case of chlorinated alkyl radicals. While the error limits of the experimental and estimated values of $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ overlap for R = CH_2Cl and R = $CHCl_2$ (uncertainties in the GA-estimated values are due to those of the experimental heats of formation of CH_2Cl and $CHCl_2$ which had to be used since GA method is inapplicable to such small radicals), the disagreement in the cases of R = CH_3CHCl and R = CH_3CCl_2 is larger than the experimental uncertainties. This disagreement can be attributed to a higher uncertainty in the group contribution values of chlorinated hydrocarbons; an uncertainty that reveals itself, for example, in similar disagreement between the experimental and GA-estimated values of the heats of formation of the CH_3CHCl and CH_3CCl_2 radicals. $\Delta H_f°_{298}(CH_3CHCl) = 76.5 \pm 1.6$ kJ mol^{-1} from experiment and 79.5 kJ mol^{-1} from GA; $\Delta H_f°_{298}(CH_3CCl_2) = 48.4 \pm 7.6$ kJ mol^{-1} from experiment and 57.3 kJ mol^{-1} from GA (if the radical group contribution values of Dilling[24] are used). Group additivity values of $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ for R = CCl_3 and R = $(CH_3)_2CCl$ could not be calculated due to the unavailability of the appropriate group values.

Heats of Formation of RO_2 and ROOH. Experimental data on $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ in Table 3 were used in conjunction with known heats of formation of corresponding R radicals to obtain the enthalpies of formation of the RO_2 peroxy radicals. The results are presented in Table 4. The heats of formation of the corresponding hydroperoxides (ROOH) were calculated using the hydrogen bond increment method[35] with the $DH°_{298}(ROO-H) = 366$ kJ mol^{-1} derived by Stocker and Pilling[28] (which is in reasonable agreement with 370.7 ± 2.5 kJ mol^{-1} recommended by Benson[12]). The uncertainty in $DH°_{298}(ROO-H)$ is taken as ±3 kJ mol^{-1} (maximum deviation of values for individual ROOH molecules considered by Stocker and Pilling). The evaluated values of $\Delta H_f°_{298}(ROOH)$ are in good agreement with the few available experimental and theoretical ones (Table 4). Error limits of the heats of formation of ROOH and RO_2 reported in Table 4 are obtained by adding the experimental uncertainties of $\Delta H_f°_{298}(R)$, $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$, and the estimated uncertainty in $DH°_{298}(ROO-H)$.

Summary

Earlier laser photolysis/photoionization mass spectrometry experimental results on the kinetics of relaxation to equilibrium in $R + O_2 \rightleftarrows RO_2$ systems (R = CH_3, C_2H_5, i-C_3H_7, t-C_4H_9, CH_2Cl, $CHCl_2$, and CCl_3) are reanalyzed using an improved kinetic mechanism[9] which accounts for further reactions of the RO_2 adduct. This analysis yields corrected temperature dependencies of the equilibrium constants of the addition reactions, $K_P(T)$. Third-law treatment is used to obtain the values of the reaction enthalpy $\Delta H°_{298}(R + O_2 \rightleftarrows RO_2)$ from the experimental $K_P(T)$ data. Literature data and ab initio calculations of the molecular properties of *i*-$C_3H_7O_2$ and *t*-$C_4H_9O_2$ radicals are used to obtain the necessary thermodynamic functions.

It is shown that enthalpy of the addition reactions of alkyl and chloroalkyl radicals with molecular oxygen can be represented by a linear function of the numbers of C−C ($N_{\mathrm{C-C}}$) and C−Cl ($N_{\mathrm{C-Cl}}$) bonds at the C atom forming the C−O bond:

$$-\Delta H^\circ_{298}(\mathrm{R} + \mathrm{O}_2 \rightleftarrows \mathrm{RO}_2) = \mathrm{H}_{\mathrm{CH}_3} + h_{\mathrm{C-C}}\mathrm{N}_{\mathrm{C-C}} + h_{\mathrm{C-Cl}}\mathrm{N}_{\mathrm{C-Cl}} \quad (\mathrm{X})$$

($H_{\mathrm{CH}_3} = 139.9 \pm 2.0$ kJ mol^{-1}; $h_{\mathrm{C-C}} = 5.7 \pm 1.1$ kJ mol^{-1}; $h_{\mathrm{C-Cl}} = -16.1 \pm 1.1$ kJ mol^{-1}).

The experimental values of $\Delta H^\circ_{298}(\mathrm{R} + \mathrm{O}_2 \rightleftarrows \mathrm{RO}_2)$ for alkyl R radicals agree with the predictions of the group additivity method within experimental uncertainties, while for chloroalkyl radicals the agreement is poor. Enthalpies of formation for RO_2 peroxy radicals and ROOH hydroperoxides (R = CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9, CH_2Cl, $CHCl_2$, CCl_3, CH_3CHCl, and CH_3CCl_2) are calculated from the experimental heats of formation of R radicals, the values of $\Delta H^\circ_{298}(\mathrm{R} + \mathrm{O}_2 \rightleftarrows \mathrm{RO}_2)$ obtained in the current study, and the hydrogen bond increment $\mathrm{D}H^\circ_{298}$(ROO−H) = 366 kJ mol^{-1} derived by Stocker and Pilling.[28]

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Supporting Information Available: Tables 1S−4S containing information on the properties of *i*-$C_3H_7O_2$ and *t*-$C_4H_9O_2$ radicals determined in the ab initio study (10 pages). Ordering information is given on any current masthead page.

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