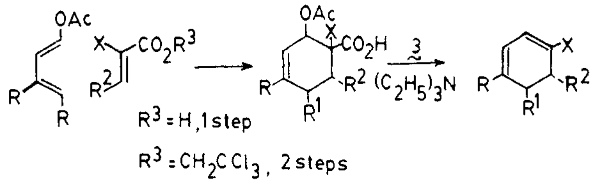
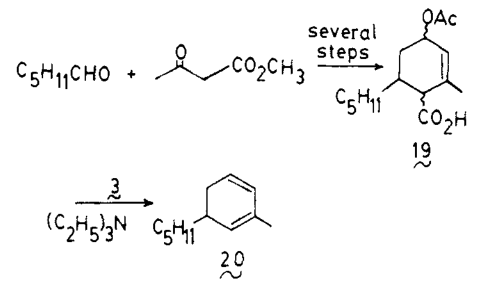
be necessary. For example, in the production of **15**, a reaction time of ~4 h sufficed; increasing the time to 18 h led to clean isomerization to methyl cyclohexa-1,4-diene-1-carboxylate[17,19e] which was isolated in 64% yield. Such an observation may be general.



diene	R	R^1	R^2	X	%
14	H	H	H	H	87
$\mathbf{15}^{19a}$	H	H	CO_2CH_3	H	71
$\mathbf{16}^{19b}$	H	C_2H_5	H	H	69
$\mathbf{17}^{19c}$	H	H	H	OAc	81
$\mathbf{18}^{17,23}$	CH_3	H	Ph	H	77
$\mathbf{19}^{19b}$	H	H	C_2H_5	H	69



Thus, this stereocontrolled diene synthesis represents a prototype fragmentation reaction catalyzed by palladium. It is interesting to note that loss of CO_2 to form diene is faster than loss of a proton to form a dienecarboxylic acid. Thus, this reaction complements the previous diene synthesis.[22] We attribute the high to exclusive stereocontrol observed to the complexation of the allyl cation by palladium in the intermediate which increases its lifetime and thus allows ejection of CO_2 in both a syn and anti fashion. Steric interactions presumably are responsible for formation of the *E* olefin. Thus, reactions in which the stereochemistry of the substrates determines the stereochemistry of the products is not always desirable. The present study illustrates one such case. The possibility that other fragmentation reactions may be initiated by palladium, or other transition metals, with benefits of the type reported here are under active investigation.

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Electron Affinity of HO_2 and HO_x Radicals[1]

Sir:

The $HO_2\cdot$ radical is of great importance in flames, in oxidation at both low and high temperatures, in biological systems, and in the chemistry of the atmosphere (stratosphere and troposphere).[2a] The anion of the radical HO_2^- appears very important in solution oxidations[2a] and in the aqueous chemistry of O_3. A related species HO_3^- appears to be very important in the chemistry of O_3 reactions with saturated species at temperatures below 0 °C.[2b] A recent review[3] lists a value for the electron affinity of $HO_2\cdot$ [EA($HO_2\cdot$)] of 4.6 eV. This value comes from a necessarily crude estimate made over 40 years ago. It appears to be much too high to be plausible.

There is a considerable amount of fairly reliable data available on the aqueous thermochemistry of H_2O_2 and HO_2^- [4,5] as well as on the related species HO_2 (aqueous) and

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Table I. Thermochemical Data

ref	substance (phase)	$\Delta H_f°_{298}$, kcal/mol	$S°_{298}$, cal/(mol K)
7	$H_2O_2(g)$	−32.6	55.6
7	$H_2O_2(l)$	−44.9	26.2
7	$H_2O_2(aq)$	−45.7	34.5
7	$H_2O(g)$	−57.8	45.1
7	$H_2O(l)$	−68.3	16.7
8	$HO_2(g)$	3.0 ± 0.5	54.1[a] (55.1)[b]
a	$HO_2(aq)$	−8.6 ± 1	33 ± 1
7	$O_2(g)$	0	49.0
7	$O_2(aq)$	−2.8	26.5
7	$OH(g)$	9.3	43.9
a	$OH(aq)$	−1.7 ± 0.5	23 ± 1
a	$HO_2^-(g)$	−40.3 ± 2.5[c]	53 ± 1
4, 7	$HO_2^-(aq)$	−38.3	6.5
3, 7	$HO^-(g)$	−33.7	41.2[a]
7	$HO^-(aq)$	−55.0	−2.6
3, *a*	$O_2^-(g)$	−10.1	50.4[a]
6, *a*	$O_2^-(aq)$	−5.9 ± 1	19

[a] Values estimated in this work. [b] Value estimated in ref 5 from independent data. [c] EA(HO_2) = 1.88 ± 0.11 eV (43 kcal).

O_2^- (aqueous).[6] These values together with related values on structurally similar species make it possible to make new estimates of the electron affinity of $HO_2\cdot$ with much greater reliability.

From known data on $HO_2\cdot(g)$ and $HO_2^-(aq)$ (Table I) one can estimate the sum of EA($HO_2\cdot$) and $H_{aq}[HO_2^-(g)]$:

$$e^- + HO_2(g) \overset{1}{\rightleftharpoons} HO_2^-(g) \qquad -EA(HO_2) \equiv \Delta H_1$$

$$HO_2^-(g) \overset{2}{\rightleftharpoons} HO_2^-(aq) \qquad \Delta H_{aq}[HO_2^-(g)] = \Delta H_2$$

$$e^- + HO_2(g) \overset{1,\,2}{\rightleftharpoons} HO_2^-(aq)$$

$$\Delta H_1 + \Delta H_2 = -EA(HO_2) + \Delta H_{aq}[HO_2^-(g)] \qquad (I)$$

From the data in Table I, $\Delta H_1 + \Delta H_2 = -41.3$ kcal/mol so that we can write

$$EA[HO_2(g)] = 41.3 + H_{aq}[HO_2^-(g)] \qquad (II)$$

To estimate $H_{aq}[HO_2^-(g)]$ we make use of the empirical relation, that the heats of solvation of negative ions seem to be monotonically related to their diameters.[9] Table II lists some of the relevant values. If we use O_2^- as the closest species in dimensions to HO_2^-, we could estimate a value for $\Delta H_{aq}[HO_2^-(g)] = 2 \pm 2.5$ kcal/mol. The argument for a more exothermic value than that for O_2^- would be based on the observation that $OH^-(g)$ is more strongly solvated than F^- by ~3 kcal (Table II) and HS^- is more strongly solvated than Cl^- by ~7 kcal. The actual value of $\Delta H_{aq}(O_2^-)$ suggests a value closer to that for Cl^- than to F^- for the difference but we have chosen to be conservative and allow the greater difference to appear in the uncertainty. This leads then to the value for $EA[HO_2(g)] = 43.3 \pm 2.5$ kcal/mol (1.88 ± 0.11 eV).

The value for the $\Delta H_{aq}[HO_2(g)] = -11.6 \pm 1$ kcal/mol which appears in Table I is estimated by assuming that it is approximately the average of the values for H_2O of −10.5 and for H_2O_2 of −13.1 kcal/mol. The value for $\Delta H_f°[HO_2(aq)]$ turns out to be in excellent agreement with the value of 8.0 ± 1 kcal/mol estimated from kinetic measurements on the Fe^{3+}/H_2O_2 system.[5]

If we compare the value of $EA[HO_2(g)]$ with measured values for related species shown in Table III, we see that it is quite reasonable. Based on these values we feel that it is also reasonable to estimate the electron affinities for species such as $RO_2\cdot$, $RO_3\cdot$, and $HO_3\cdot$ to be the same as $HO_2\cdot$, namely 1.85 ± 0.12 eV. Support for such an assumption is to be found in the pK_{ion} values of hydroperoxides[11] which tend to fall within ±0.5 p*K* units of $pK_{ion}(H_2O_2)$. This suggests that the differences in solvation enthalpies of $RO_2\cdot$ and RO_2H must be within ~0.7 kcal of that for $HO_2\cdot$ and HO_2H. It is a situation which finds a striking parallel in the pK_{ion} values of the carboxylic acids.[12]

Table II. Enthalpies of Aquation of Some Gas-Phase Anions

anion	$\Delta H°_{aq}$, kcal/mol	anion	$\Delta H°_{aq}$, kcal/mol
OH^-	−21.3	HS^-	12
F^-	−18.0	NO_2^-	
H^-	−16.0[a]	CN^-	9
Cl^-	18.9	O_2^-	4
Br^-	27	HO_2^-	2 ± 2.5[b]
I^-	34		

[a] Estimated by using a dimension for H^- anion from crystal anion-cation distances and comparing them with those of alkali halides. It leads to a value of $\Delta H_f°_{298}[H^-(aq)] = 34$ kcal/mol. [b] Estimated in this paper.

Table III. Electron Affinities of Some Oxy Radicals

ref	radical	EA, eV
3	O_2	0.44
3	O	1.46
3	OH	1.83
3, 10	CH_3O	1.8 ± 0.1
3, 10	*n*-PrO	1.9 ± 0.1
a	HO_2	1.85 ± 0.12
10	O_3	2.89
a	RO_2	1.85 ± 0.12

[a] Estimated here. R is taken as an alkyl group.

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Hemoprotein Models: NMR of Imidazole Chelated Protohemin Cyanide Complexes

Sir:

^1H NMR studies of low-spin ferric ($S = 1/2$) cyanide complexes of hemoproteins have shown the heme methyl resonances to be differentially hyperfine shifted so as to spread them from 8 to 28 ppm downfield of their diamagnetic positions.[1-7] By contrast, the biscyanide complex of protohemin

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