THERMOCHEMICAL PARAMETERS FOR MOLECULES AND REACTION INTERMEDIATES CONTAINING THE DIPHENYLMETHYL MOIETY

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Detailed thermodynamic data for species containing the [Ph_2C] group are reported. The values were obtained by critical evaluation of literature data, combined with analysis and estimation of unavailable parameters. The resulting set of values includes stable molecules and intermediates such as $Ph_2CH^{\bullet}$, $Ph_2C^{\bullet\bullet}$, $Ph_2C^{\bullet}OH$, Ph_2COO, Ph_2CH^{+}, $Ph_2CH^{+\bullet}$, Ph_2CH^{-} and $Ph_2CH^{-\bullet}$, and should provide a solid base for the estimation of thermochemical changes and redox potentials in reactions involving these species.

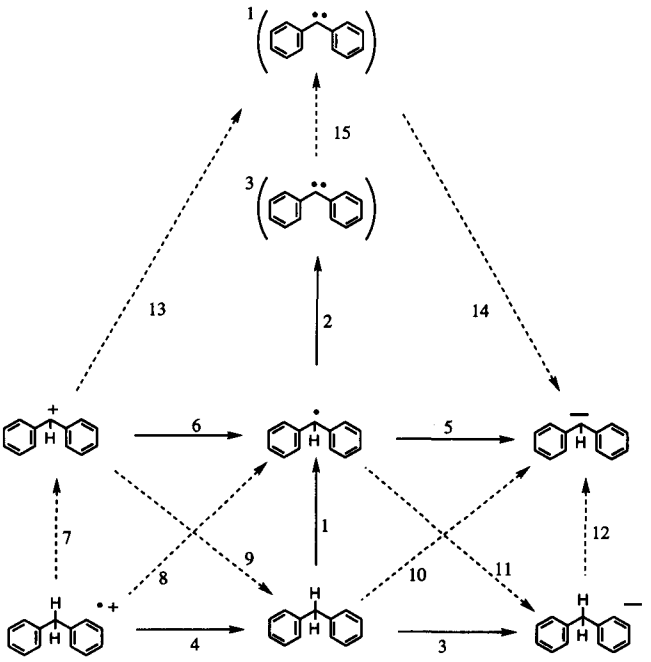
Keywords: thermochemical calculations; fred radicals; diphenylmethyl radicals.

1. INTRODUCTION

The diphenylmethyl moiety is one of the most common groups in molecules used in mechanistic studies of reaction intermediates and in photochemistry. Thus, diphenyl carbene, diphenylmethyl radical, diphenylmethyl cations, benzophenone oxide and the triplet state of benzophenone figure prominently in reports on organic reaction mechanisms.

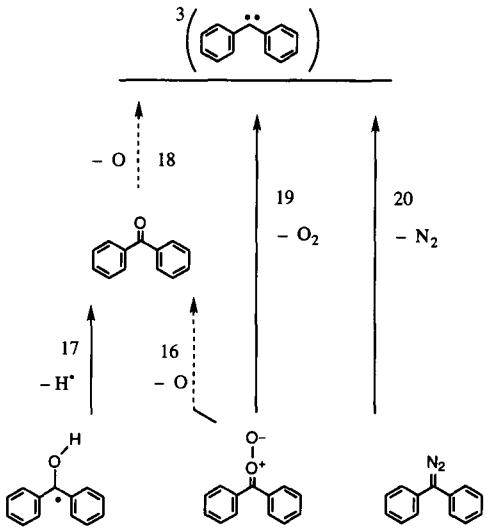
During the last decade there have been several reports that considerably improve our understanding of the kinetics, mechanisms and thermochemical parameters of these species. These, combined with long established parameters (e.g. some enthalpies of formation, energies of phophorescent states, etc.) should allow one to construct a thermodynamic cycle providing a solid basis for thermochemical calculations. In principle one should be able to estimate the enthalpies/free energies of formation of all the molecules and reaction intermediates involved. While available in the literature, many parameters are widely scattered in many reports and it is frequently difficult to establish which values form part of a consistent set, in terms of both the assumptions involved, as well as the experimental conditions used.

Recent work[1,2] describes how thermodynamic properties of ions and radicals can be related in a thermodynamical cycle if a certain number of bond dissociation energies and electrode potentials are known. In an approach similar to that used in the review by Wayner and Parker[1] we can represent the relationship between the various thermodynamic properties of the ions and radicals containing the diphenylmethyl moiety by the thermochemical mnemonic shown in Scheme I. Horizontal arrows represent redox processes, with reduction always from left to right, the vertical lines represent bond dissociations, the diagonal lines to the left represent the addition of H^- and the diagonal lines to the right represent H^+ dissociation. The latter processes can be related to pK_h (dissociation of H^-) and pK_a values, respectively. The continuous arrows represent reactions for which we will select values from the experimental data. This is the minimum set of processes for which thermochemical data are needed to calculate the thermochemical parameters for all the remaining reactions (dashed arrows). Besides compiling and calculating thermochemical data for the reactions shown in Scheme I, we also include reactions involving benzophenone, diphenyldiazomethane, and related intermediates (Scheme II).



Scheme I. Thermochemical mnemonic describing heterolytic and homolytic reactions of molecules involving the diphenylmethyl moiety.

To produce a consistent data base one needs a set of experimental conditions which will be useful for potential users of the data, and for which the literature provides sufficient information. Our set of "standard" conditions corresponds to dry acetonitrile at 298 K. This is a solvent frequently used in electrochemical studies of charged intermediates and for which it is not unreasonable to assume that data relating to uncharged intermediates [e.g. bond dissociation energy in $Ph_2C(H)—H$] will not be largely influenced by polarity. All electrode potentials employed throughout this analysis are quoted with reference to the normal hydrogen electrode, $(NHE)_{aq}$. However, most electrochemical data was reported for SCE as the reference electrode. The standard conversion of + 0.24 V of SCE vs. $(NHE)_{aq}$ was used throughout.



Scheme II. Reactions involving compounds with the benzophenone moiety.

The main difficulty in compiling these data derives from the fact that thermochemical measurements normally lead to enthalpy changes, while electrochemical studies lead to free energies. Combining these data requires some knowledge of entropies for reaction intermediates; some of these, such as solubilization entropies or free energies for some short lived intermediates (e.g. hydrogen or oxygen atoms) are not available from experiments.

Clearly, some of the values will be subject to future revision. While data from different original reports quote different error limits, we feel that their combined result should be consistent to within ± 2 kcal mol^{-1}. Values derived directly from these probably have comparable error limits, but when multiple steps are involved it is easy to see that errors may tend to accumulate. In Table I we provide the detailed formulae employed in each calculation, which should enable the reader to judge the validity of each approximation. Further, it should be straightforward to update the estimates as new data become available or as older measurements are further refined.

2. TECHNIQUES EMPLOYED TO OBTAIN THERMOCHEMICAL AND ELECTROCHEMICAL DATA

The two principal parameters needed to describe thermodynamic cycles involving intermediates such as radicals, radical ions, cations and anions are bond dissociation energies (BDE) and electrode potentials for the reduction and oxidation processes. In addition, entropic parameters are needed to relate thermochemical (ΔH) and electrochemical (ΔG) values.

Obtaining reliable data for bond dissociation energies is not a trivial enterprise, specially when dealing with short lived reaction intermediates. Several classical methods are employed to measure BDE in the gas phase, such as shock tube methods, iodination reactions and very low pressure pyrolysis; these rely on kinetic measurements which are then related to the heat of formation of the free radical and BDE values of stable compounds. All these methods require a keen awareness of the underlying assumptions. For example, the iodination reaction method assumes that hydrogen abstraction by the alkyl

Table I. Calculations leading to the thermodynamic values in Table II and corresponding to the steps in Schemes I and II. The numeric sequence has been modified slightly to emphasize a convenient order for the calculations.

Step	Source
1	ΔH_1 experimental ; $\Delta G_1 = \Delta H_1 - S\ (H^\bullet)_{cor}$
2	$\Delta H_2 = \Delta H_f(Ph_2C\bullet\bullet) + \Delta H_f(H^\bullet) - \Delta H_f(Ph_2CH\bullet)$; $\Delta G_2 = \Delta H_2 - S\ (H^\bullet)_{cor}$
3	E_0 estimated as similar to toluene
4	E_0 experimental
5	E_0 experimental
6	E_0 experimental
9	$\Delta G_9 = \Delta G_6 - \Delta G_1 - \Delta G(H^\bullet/H^-)$
7	$\Delta G_7 = \Delta G_4 - \Delta G_9 - \Delta G(H^\bullet/H^-)$
8	$\Delta G_8 = \Delta G_4 + \Delta G_1 - \Delta G(H^+/H^\bullet)$
10	$\Delta G_{10} = \Delta G_1 + \Delta G_5 - \Delta G(H^+/H^\bullet)$
11	$\Delta G_{11} = \Delta G_3 - \Delta G_1 - \Delta G(H^\bullet/H^-)$
12	$\Delta G_{12} = \Delta G_{10} - \Delta G_3 + \Delta G(H^+/H^\bullet)$
13	$\Delta G_{13} = \Delta G_6 + \Delta G_2 + \Delta G_{15} - \Delta G(H^+/H^\bullet)$
14	$\Delta G_{14} = -\Delta G_2 - \Delta G_{15} + \Delta G_5 - \Delta G(H^\bullet/H^-)$
15	ΔH_{15} estimated (see text); $\Delta G_{15} = \Delta H_{15} + RT\ln(3)$
17	$\Delta H_{17} = \Delta H_f(Ph_2O) + \Delta H_f(H\bullet) - \Delta H_f(Ph_2OH\bullet)$; $\Delta G_{17} = \Delta H_{17} - 4.8$ kcal/mol
16	$\Delta H_{16} = 0.5[\Delta H_{23} + BDE(O_2)]$, or $\Delta H_{16} = \Delta H_f(Ph_2CO) - \Delta H_f(Ph_2COO) + \Delta H_f(O)$
	$\Delta G_{16} = \Delta H_{16} - T(S^0_{gas}(O) + \Delta S_{solub}(O)$; see text for discussion of ΔH_{16}.
20	ΔH_{20} experimental, $\Delta G_{20} = \Delta H_{20} - T(S^0_{gas}(N_2) + \Delta S_{solv}(N_2))$
19	$\Delta H_{19} = \Delta H_{20} - \Delta H_{24}$, $\Delta H_{24} = -48.1$ (experimental)
	$\Delta G_{19} = \Delta H_{19} - T(S^0_{gas}(O_2) + \Delta S_{solub}(O_2))$
18	$\Delta H_{18} = \Delta H_{19} - \Delta H_{16} + BDE(O_2)$, $\Delta G_{18} = \Delta H_{18} - T(S^0_{gas}(O) + \Delta S_{solub}(O))$

radicals from HI is a non activated process; in the shock tube approach data collected at very high temperatures are extrapolated to 300K; the very low pressure pyrolysis technique is only reliable if care is taken to carefully coat the surface of the vessels to avoid reaction with the walls. The most critical drawback of these techniques is that the data relate to the gas phase and our purpose is to establish a thermodynamical cycle for transients in solution.

Several techniques have been employed to measure heats of formation in solution. Electron paramagnetic resonance (EPR) was used to follow radical concentrations in the exchange reaction between alkyl radicals and alkyl iodides (radical buffer measurement). The heat of formation of the radical is obtained from equilibrium concentrations and literature values for the alkyl halides thermodynamic parameters. This method has been employed to establish the heats of formation of simple alkyl radicals. Its application is limited to highly reactive radicals.[3-5]

Laser Induced Optoacoustic (or Photoacoustic) Calorimetry (LIOAC) makes it possible to determine enthalpic changes associated with rapid processes. In particular it allows the determination of parameters for short lived reaction intermediates. Excitation of a sample by a short laser pulse results in rapid local deposition of heat. This release of energy generates an acoustic wave that can be monitored with a suitable pressure sensitive detector. Since the heat released is a function of energy uptake or release by the reaction (i.e. of ΔH), enthalpic terms can be obtained by quantitative analysis of LIOAC data. The technique has been recently reviewed.[5-8]

The determination of electrochemical parameters for transient intermediates, such as radicals in solution requires special considerations. The gas phase parameters, electron affinity and ionization potentials are not directly applicable to reactions in solution. Oxidation and reduction potentials of radicals can be measured from the electrochemistry of the corresponding cations or anions, but only few of these ions can be sufficiently stabilized for electrochemical measurements. In some cases the conditions to stabilize the ions, e.g. highly acidic solutions for cations, make the resulting potentials of limited value for studies in more common solvents, such as acetonitrile. Electrochemical potentials have been obtained by studying the radicals with photomodulation voltammetry. The radicals are photochemically generated by a modulated light source. The output of the potentiostat is fed into a lock-in amplifier that is referenced to the chopping frequency of the light source. Thus, the electrochemical response due to the radical is enhanced in relation to noise[5]

3. DISCUSSION OF THE SELECTION CRITERIA FOR LITERATURE VALUES AND RATIONALE FOR THE CALCULATION OF ESTIMATED THERMOCHEMICAL PARAMETERS

To calculate the thermodynamical parameters for the processes in Scheme I we need to know the heat and free energy of formation of H$^\bullet$ and the values for $E^\circ(H^+/H^\bullet)$ and $E^\circ(H^\bullet/H^-)$ in acetonitrile. An analysis in which the free energies of solvation of noble gases is correlated to the free energy of solvation of H$^\bullet$ has shown that one cannot assume that the free energy of formation of the hydrogen atom is the same in the gas phase and in different solvents.[9,10] The values reported are: $\Delta G_f(H^\bullet)_{ACN}$ = 54.3 kcal/mol, $E^\circ(H^+/H^\bullet)_{ACN}$ *vs.* $(NHE)_{aq}$ = −1.77 V and $E^\circ(H^\bullet/H^-)_{ACN}$ *vs.* $(NHE)_{aq}$ = −0.60 V. We note that the $E^\circ(H^+/H^\bullet)_{ACN}$ value used corresponds to that recently reported in a correction by Parker[10] and not that appearing in earlier reports.[9,11] Free energies for hydrogen atom solvation have been estimated by Parker[11] on the basis of a comparison with the noble gases. In our case we find that enthalpic corrections are small enough that within the ± 2 kcal/mol error limits they can probably be ignored. Thus, for the enthalpy of formation of H$^\bullet$ we use the gas phase value of 52.1 kcal/mol. For X-H bond energies in acetonitrile we introduce the correction proposed by Wayner and Parker[1] related to the free energy of solvation and entropy change due to H$^\bullet$ formation; i.e. bond dissociation energies involving H exceed ΔG values by 4.8 kcal/mol.

The reduction and oxidation of the diphenylmethyl radical was studied by photomodulation voltammetry[12]. The values are: $E^\circ(Ph_2CH^\bullet/Ph_2CH^-)$ = -0.90 V *vs.* $(NHE)_{aq}$ [original value: -1.47 V *vs.* $Ag/AgNO_3$ (0.1 M in ACN) which was in turn reported to have a potential of 0.334 V *vs.* SCE] and $E^\circ(Ph_2CH^+/Ph_2CH^\bullet)$ = 0.59 *vs.* $(NHE)_{aq}$ [original data: + 0.02 V in $Ag/AgNO_3$ (0.1 M in ACN)] (Table II).

The oxidation potential of diphenylmethane ($E^\circ(Ph_2CH_2^{\bullet+}/Ph_2CH_2)$) was determined to be 2.25 V *vs.* $(NHE)_{aq}$ (original determination *vs.* SCE).[13] Since we could not find a value for the reduction of diphenylmethane we assume a value of -3.1 V *vs.* $(NHE)_{aq}$ that is close to the value for toluene (Table II).

The heat of formation of diphenylmethane is 33.2 kcal/mol (Table III).[14] The heat of formation of diphenyldiazomethane, that is necessary for the calculation of the heat of formation of the diphenyl carbene was evaluated from step # 21 (Note that reactions with step # greater that 20 are given in the text, not the tables).

$$Ph_2CN_2 + Et(OH) \longrightarrow Ph_2CHOEt + N_2 \qquad \text{Step \# 21}$$

ΔH for reaction 21 was measured by LIOAC calorimetry and corresponds to -53.6 kcal/mol.[14] The heat of formation of Ph_2CHOEt (-10.6 kcal/mol) was estimated from group additivity contributions[15] and the value for ΔH_f of ethanol is -56.2 kcal/mol.[16] From these values a heat of formation of 99.2 kcal/mol was calculated for diphenyldiazomethane.

Thermochemical data for diphenyl carbene correspond to the triplet state and are based on photoacoustic studies of the following reaction:

$$Ph_2CN_2 \longrightarrow {}^3Ph_2C{\bullet\bullet} + N_2 \qquad \text{Step \# 20}$$

ΔH_{20} values of ~0 and -1 kcal/mol have been reported.[17,18] An earlier report giving ΔH_{20} = -12 kcal/mol[19] has now been established to be incorrect[17] and the reason for the original problems discussed in detail;[7] these difficulties illustrate well the experimental requirements of the technique. Based on the ΔH_f value for Ph_2CN_2 determined above a value of 98.2 kcal/mol was established for the enthalpy of formation of triplet diphenyl carbene. A short discussion on the relevance of the multiplicity of the carbene involved in the thermochemical cycle is in order. The decay of the singlet carbene formed in the photolysis of diphenyldiazomethane is very fast (subnanosecond)[20,21] and occurs within the time window for which heat release is being measured in the optoacoustic experiment. On the other hand, the triplet carbene is long lived compared to the detection time and is considered to be the "end product" of the reaction. However, the proton dissociation and H^- association processes that can lead to carbene formation (processes 13 and 14 in Scheme I) will yield initially the singlet carbene. For this reason thermochemical calculations must take into account the energy corresponding to the triplet-singlet splitting. Although the energy splitting between singlet and triplet carbenes has been a subject of considerable controversy, it is clear that models suggesting gaps of up to 5 kcal/mol fail to explain the temperature dependence of carbene reactions.[22] The experimental data is consistent with a somewhat larger gap. The value of 7.0 kcal/mol is assumed, since at the same time it is reasonable to expect that the gap in diphenyl carbene will be smaller than in the parent CH_2. The difference between ΔH_{15} and ΔG_{15} is based on the assumption that the only entropic difference between singlet and triplet carbenes re-

Table II. Thermodynamic parameters for each process in Schemes I and II at 298 K, in acetonitrile whenever possible.

#	From	To	ΔH (kcal/mol)	ΔG(kcal/mol)	E_0 (V)
1	Ph_2CH_2	$Ph_2CH^{\bullet}$ + $H^{\bullet}$	81.4	76.6	
2	$Ph_2CH^{\bullet}$	$^3Ph_2C$: + $H^{\bullet}$	87.8	83.0	
3	Ph_2CH_2 + e^-	$Ph_2CH_2^{-\bullet}$		71.5	(-3.1)
4	$Ph_2CH_2^{+\bullet}$ + e^-	Ph_2CH_2		-51.9	2.25
5	$Ph_2CH^{\bullet}$ + e^-	Ph_2CH^-		+20.8	-0.90
6	Ph_2CH^+ + e^-	$Ph_2CH^{\bullet}$		-13.6	0.59
7	$Ph_2CH_2^{+\bullet}$	Ph_2CH^+ + $H^{\bullet}$		38.3	
8	$Ph_2CH_2^{+\bullet}$	$Ph_2CH^{\bullet}$ + H^+		-16.1 pK_a -11.8	
9	Ph_2CH^+ + H^-	Ph_2CH_2		-104 pK_h 76.2	
10	Ph_2CH_2	Ph_2CH^- + H^+		56.6 pK_a 41.5	
11	$Ph_2CH^{\bullet}$ + H^-	$Ph_2CH_2^{-\bullet}$		-18.9 pK_h 13.9	
12	$Ph_2CH_2^{-\bullet}$	Ph_2CH^- + $H^{\bullet}$		25.9	
13	Ph_2CH^+	$^1Ph_2C$: + H^+		36.3	
14	$^1Ph_2C$: + H^-	Ph_2CH^-		-83.7 pK_h 61.4	
15	$^3Ph_2C$:	$^1Ph_2C$:	(7.0)	(7.7)	
16	Ph_2COO	Ph_2CO + O	21.5 (3.2)[a]	11.6 (-6.2)[a]	
17	$Ph_2COH^{\bullet}$	Ph_2CO + $H^{\bullet}$	35	30.2	
18	Ph_2CO	$^3Ph_2C$: + O	144.6 (162.9)[a]	135.6 (153.9)[a]	
19	Ph_2COO	$^3Ph_2C$: + O_2	47.1	37.3	
20	Ph_2CN_2	$^3Ph_2C$: + N_2	-1	-9.9	

[a] See text for a discussion of these values.

Table III. Basic thermodynamic parameters for the species involved in the thermodynamic calculations for the reactions in Schemes I and II.

Species or Couple	ΔH_f , kcal/mol	S_0, cal/K mol	ΔG_f, kcal/mol	R^0_{red}/NHE
H+/H•			40.8	-1.77 V
H•/H–			+13.8	-0.60 V
H•	52.1		54.3	
N_2	0	45.8 (gas)	–13.6 (gas)	
O_2	0	49.0 (gas)	–14.6 (gas)	
O	59.5	38.5 (gas)	48.0 (gas)	
Ph_2CH_2	33.2			
$Ph_2CH^{\bullet}$	62.5			
$^3(Ph_2C:)$	98.2			
Ph_2CN_2	99.2			
Ph_2COO	51.2			

flects their relative multiplicity, thus, its contribution to the free energy difference is: $\Delta\Delta G \sim RT\ ln(3)$.

A value of 81.4 kcal/mol has been established for the bond dissociation energy of diphenylmethane in very low pressure pyrolysis experiments.[23] This experimental value is very close to a recently calculated one (80.6 kcal/mol).[24] The bond dissociation energy value leads to a ΔH_f value for the diphenylmethyl radical of 62.5 kcal/mol [$\Delta H_f(Ph_2CH^{\bullet}) = BDE(Ph_2CH_2) - \Delta H_f(H^{\bullet}) + \Delta H_f(Ph_2CH_2)$].

The BDE for the diphenylmethyl radical is calculated from the reaction:

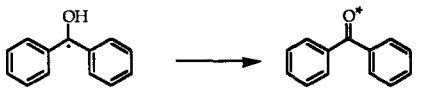
$Ph_2CH^{\bullet} \longrightarrow Ph_2C^{\bullet\bullet} + H^{\bullet}$ Step # 2

where the BDE is given by $BDE(Ph_2CH^{\bullet}) = \Delta H_f(Ph_2C^{\bullet\bullet}) +$

$\Delta H_f(H^\bullet)$ - $\Delta H_f(Ph_2CH^\bullet)$ and has a value of 87.8 kcal/mol.

As expected the value for the dissociation of the second hydrogen of diphenylmethane to form the carbene is energetically less favorable than the dissociation that leads to the formation of the radical.

Two values have been reported for the O-H bond in the ketyl radical $Ph_2C^\bullet OH$. These are 110 kcal/mol[25] and 95 kcal/mol[26]. The latter is probably based on too low a bond dissociation energy for ethanol;[27,28] an appropriate correction leads to a bond energy of 97 kcal/mol in the ketyl radical. Not being sure which value to select, we tentatively take the average, or ~104 kcal/mol for:



Step # 22

leading to a ΔH of 35 kcal/mol for step # 17, which corresponds to the BDE given above for step # 22 corrected to take into account the triplet excitation energy of benzophenone (Table IV).

Table IV. Excited state energies for selected reaction intermediates from Schemes I and II

Species	Type	Excitation Energy (kcal/mol)
Ph_2CO	triplet	69.0
$Ph_2C^{\bullet\bullet}$	triplet	56.7
$Ph_2CH^\bullet$	doublet	54.3
$Ph_2C^\bullet OH$	doublet	(51)[a]

[a] 0,0 band not resolved.

We could not locate an enthalpy of formation for benzophenone in acetonitrile, although a value of -5.2 kcal/mol has been reported in benzene.[25] This value is based on the heat of formation of crystalline benzophenone corrected to account for the solubilization heat.[25] If this value is used, one obtains the values in parenthesis for steps # 16 and 18 (Table II). An alternate approach to those steps is provided by the enthalpy for step # 23 (ΔH_{23} = –76.0 ± 4.0 kcal/mol) reported by Hartstock et al.[14]

$$2\ Ph_2COO \longrightarrow 2\ Ph_2CO + O_2 \qquad \text{Step \# 23}$$

from step # 23 one can derive: $\Delta H_{16} = 0.5\ [\Delta H_{23} + BDE(O_2)]$, which yields ΔH_{16} = +21.5 kcal/mol. This in turn leads to ΔH_{18} = 144.6 kcal/mol. While we cannot pinpoint the origin of the discrepancy, we suspect that its origin resides in the enthalpies of formation for benzophenone. If this is the case, further refinement of the numbers should be possible. Given that carbonyl oxides are very long lived,[29] we tentatively prefer ΔH_{16} = +21.5 kcal/mol. In the case of step # 18 the process is so unfavorable that either value could predict the stability of benzophenone.

The change in enthalpy for reaction 24 was determined by LIOAC to be -48.0 kcal/mol.[14] The value for the heat of formation of the benzophenone oxide can be derived from this experimental result ($\Delta H_f(Ph_2COO) = \Delta H_{24} - \Delta H_f(Ph_2CN_2)$) and corresponds to 51.2 kcal/mol

$$Ph_2CN_2 + O_2 \longrightarrow Ph_2COO + N_2 \qquad \text{Step \# 24}$$

Entropic parameters for O_2 and N_2 in the gas phase are readily available. The values at 298 K were taken as $S°_{gas}(O_2)$ = 49.0 e.u. and for N_2, $S°_{gas}(N_2)$ = 45.8 e.u.[30] Entropies of solubilization for oxygen are available in a number of solvents,[31] but not in acetonitrile. Examination of the literature shows that for polar solvents of dielectric constants comparable to acetonitrile typical values are around –16 e.u. We have assumed that this value is applicable to both, molecular oxygen and nitrogen. Typical enthalpies of solubilization for oxygen are around -0.3 kcal/mol and have been ignored in our calculations.[31] The situation is more complex in the case of atomic oxygen where parameters such as solubilization entropies are not available, and are not likely to become available in the near future. Here again we make some approximations based on the compilation from Battino.[31] While values are not available for the solubilization of atomic oxygen, sufficient data are available on oxygen and ozone that their entropies can be calculated.* We further assume that the entropic variations in the O, O_2 and O_3 series will occur at even intervals, which allows the extrapolation for O from the two available parameters. An analysis of the available data suggests then that the solubilization entropy for O will be 40-45% of the value for O_2, corresponding to $\Delta S_{solub}(O) \sim -7$ e.u. for acetonitrile. While we realize that this is only a rough approximation, at the same time, we note that 7 e.u. corresponds to about 2 kcal/mol contribution to the free energy at 298 K. Even 50% error will not affect our estimates dramatically.

4. EXAMPLES OF DETAILED CALCULATIONS

Most processes in Scheme I indicated by dashed arrows are calculated from the thermodynamic data for the processes indicated by full arrows. The elementary processes necessary to describe the reactions of interest are added or subtracted as required. The expression for each step in Schemes I and II are shown in Table I. We will show detailed examples for steps 7 and 13.

The elementary processes required to describe step 7 are shown in Scheme III.

$$Ph_2CH_2^{\bullet+} + e^- \longrightarrow Ph_2CH_2 \qquad \Delta G_4$$

$$Ph_2CH_2 \longrightarrow Ph_2CH^+ + H^- \qquad -\Delta G_9$$

$$H^- \longrightarrow H^\bullet + e^- \qquad -\Delta G(H^\bullet/H^-)$$

$$\underline{\text{Sum:}}\quad Ph_2CH_2^{\bullet+} \longrightarrow Ph_2CH^+ + H^\bullet \qquad \Delta G_7$$

Scheme III

The value for the free energy of step 7 corresponds to: $\Delta G_7 = \Delta G_4 - \Delta G_9 - \Delta G(H^\bullet/H^-)$.

The elementary steps required to describe step 13 are shown in Scheme IV.

$$Ph_2CH^+ + e^- \longrightarrow Ph_2CH^\bullet \qquad \Delta G_6$$

$$Ph_2CH^\bullet \longrightarrow {}^3Ph_2C^{\bullet\bullet} + H^\bullet \qquad \Delta G_2$$

$${}^3Ph_2C^{\bullet\bullet} \longrightarrow {}^1Ph_2C^{\bullet\bullet} \qquad \Delta G_{15}$$

$$H^\bullet \longrightarrow H^+ + e^- \qquad -\Delta G(H^+/H^\bullet)$$

$$\underline{\text{Sum:}}\quad Ph_2CH^+ \longrightarrow {}^1Ph_2C^{\bullet\bullet} + H^+ \qquad \Delta G_{13}$$

Scheme IV

* Where the values are not available, the entropies can be determined from the temperature dependence of Henry's coefficient,[31] from a plot of $-RT\ ln(\underline{x})$ against T, where $\underline{x}$ is Henry's coefficient, i.e.

$$\Delta H_{solub} - T\Delta S_{solub} = RT\ ln(\underline{x})$$

Similarly, $\Delta G_{13} = \Delta G_6 + \Delta G_2 + \Delta G_{15} - \Delta G(H^+/H^\bullet)$. The pK_a value for this reaction is equal to $\Delta G_{13}/(2.303RT)$.

5. CONCLUSION

Tables I-IV provide a solid basis for the estimation of thermochemical and electrochemical parameters for a wide range of reaction intermediates containing the [Ph_2C] group. For example, the higher reactivity of the triplet carbene with respect to the radical in hydrogen abstraction processes[32] becomes a natural consequence of the differences in bond energies (See steps # 1 and # 2 in Table II). Similarly, photochemical cleavage of $Ph_2C^\bullet OH$ to yield hydrogen atoms[33] reflects the fact that only 35 kcal/mol are required to induce this process. Even in the case of our most uncertain values (steps # 16 and # 18), one would expect carbonyl oxides to be very photolabile (step # 16). Benzophenone is unlikely to give up its oxygen atom, but triplet carbenes are known to abstract oxygen readily from nitroxides;[34] step # 18 explains this quite readily.

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