Application of the Marcus Theory on the Reaction of Substituted Dibenzoyl Peroxides with Hydroquinones: Evidence for an Inner-Sphere Electron Transfer (ET) Mechanism

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The reaction of several substituted dibenzoyl peroxides **1** with methyl-substituted hydroquinones **2** gives exclusively the corresponding benzoic acids **3** and quinones **4** as the two-electron redox products. The spectrophotometrically determined rate constants of this reaction exhibit a small solvent effect, i.e. rate acceleration with increasing solvent polarity. Furthermore, it has been shown that the kinetics depend strongly on the substituents of the dibenzoyl peroxides as well as on the one-electron oxidation potentials of the hydroquinones $E^0(HQ^\bullet/H_2Q)$. A Hammett plot gives $\varrho = +1.8 \pm 0.2$ ($r > 0.97$), which indicates accumulation of negative charge on the dibenzoyl peroxide in the transition state. Good linear semilogarithmic plots of $\log k_2$ versus $E^0(HQ^\bullet/H_2Q)$ with slopes of 17 eV^{-1} were observed for this redox process. A nonlinear statistical treatment of the kinetic data against the hydroquinone one-electron oxidation potentials according to the Marcus theory affords a consistent set of one-electron reduction potentials for the substituted dibenzoyl peroxides and the reorganization energies λ for the redox process. The $E^0(ROOR/RO^\bullet RO^-)$ values range between 150 mV for the 4-NO_2 to 47 mV for the 4-MeO derivatives. A well-fitting ($r = 0.996$) Hammett plot of $E^0(ROOR/RO^\bullet RO^-)$ versus σ values provides a slope of 100 mV per σ unit. The reorganization energy of ca. 17 ± 3 kcal mol^{-1} speaks for an inner-sphere electron transfer (ET).

The concept of electron transfer, the roots of which lie in the field of inorganic chemistry, has during the last decades become of growing importance also for organic reactions[1]. An increasing number of reactions, which have been thought to occur by ionic pathways, have been found to involve electron transfer chemistry[2]; however, the distinction between these two mechanistic alternatives is often quite subtle[3]. A classical and one of the most extensively studied redox process is the reaction between organic peroxides and various nucleophiles such as amines[4], phenols[5], methoxybenzenes[6] and olefins[7]. The products of these reactions strongly depend on the nature of the electron donor, namely the nucleophile. Although redox products are formed by oxygen transfer from the peroxide to the donor, in most cases combination products of the peroxide with the donor are observed.

By means of product studies and kinetics it has been difficult to distinguish conclusively between the mechanisms of nucleophilic displacement (S_N2) and single-electron transfer (SET)[6–8]. The proposed bimolecular electron transfer reactions of organic peroxides are of mechanistic interest in the oxidation of electron-rich aromatic substrates by molecular oxygen and active oxygen species in general, which plays a significant role in bioorganic chemistry[9].

A theoretical framework for understanding electron transfer or redox reactions is provided by the Marcus theory[10]. This is a quadratic free energy ($\log k_2$ versus ΔG^0) relationship (QFER), which allows the determination of the redox potentials and reorganization energies. The latter represent the free energy change for bond and solvent reorganization in the transition state of the redox process. In favorable cases, the Marcus treatment of rate data permits a mechanistic distinction between inner- and outer-sphere mechanisms[11].

The Marcus theory was originally developed for inorganic outer-sphere ET processes[10,12]; nevertheless, nowadays it finds also extensive applications for organic redox reactions[1], for which outer-sphere ET is, however, rare. As long as the electron transfer step is reversible, the majority of cases conform also for these cases reasonably well to the Marcus theory. In the case of irreversible redox processes, which are observed quite frequently in organic chemistry, the use of the Marcus theory is often problematic. However, for several examples, such as the oxidation of carboxylates[13] and the reduction of alkyl halides[14] and diaroyl peroxides[8b,15], the Marcus treatment gave reliable redox potentials and reorganization energies.

For the determination of redox potentials electrochemical methods cannot be generally used, because of the often low stability and thus limited persistence of the one-electron redox products. One is obliged to resort to indirect determination, for which in principle two methods are applicable. One of them is the use of thermodynamic calculations according to $\Delta G^0 = -nF(E_A - E_D)$, in which ΔG^0 is the standard free energy change for the redox process, n the number of electrons transferred ($n = 1$ for our purposes), and E_A and E_D are the reduction potential (E_{red}) of the acceptor and oxidation potential (E_{ox}) of the donor. The difficulty of this indirect method derives from reliably estimating the correction terms for solvent interaction. For example, the reduction potential (E_{red}) of dibenzoyl peroxide (**1d**) was calculated[16] to be 0.88 V in water, ca. 0.0 V in acetonitrile, and 0.65 V in dichloromethane. For comparison, the irreversible reduction potential, obtained polarographically ($E_{1/2}$) in benzene/methanol, was ca. 0.1 V for dibenzoyl peroxide (**1d**)[17].

The use of the Marcus expression [cf. Eq. (2)–(5); Results] constitutes the second alternative for an indirect determination of E^0 values for dissociative electron transfer reactions[18]. Although the Marcus theory is based on the assumption of outer-sphere ET, it is shown that it applies even for inner-sphere ET reactions, provided that the λ parameter is a constant[11]. From the experimental kinetic data, the desired E^0 and λ values for the redox process in question

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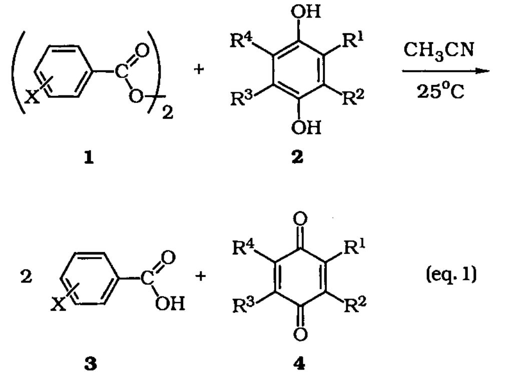
are obtained from the Marcus equation, the so-called Marcus plot (cf. Results), by nonlinear regression analysis. Reasonable Marcus plots with $\lambda = 40$ kcal mol^{-1} were observed[1b] for the redox reactions between diacyl peroxides and olefins, amines, etc. as electron donors[7,19]. The thermodynamically calculated and solvent-adapted E_{red} value of 0.65 V[1b,7,16,19] was chosen for this purpose. For the reduction of dibenzoyl peroxide (**1d**) and *tert*-butyl perbenzoate by singlet excited states, E_{red} values of 0.2 V for dibenzoyl peroxide (**1d**) and −0.95 V for *tert*-butyl perbenzoate[1b] were used.

The limited data imply that further work is needed to establish more reliable values for E_{red} and the λ parameter of acyl peroxides, in the hope of understanding more fully the mechanistic details of the irreversible ET reactions of such peroxides. For this reason we have investigated the redox reactions between a series of substituted dibenzoyl peroxides and methyl-substituted hydroquinones. Indeed, with the help of the Marcus treatment of the rate data acquired herein, a consistent set of E_{red} and λ values for diaroyl peroxides has been determined, which provide evidence for an inner-sphere ET process.

Results

Products

The reaction of stoichiometric amounts of dibenzoyl peroxides **1** and hydroquinones **2** in acetonitrile solutions at 25°C under argon afforded exclusively benzoic acids **3** and quinones **4** [Eq. (1)].



1	X
a	4-NO_2
b	3-Cl
c	4-Cl
d	H
e	4-Me
f	4-MeO

2	R^1	R^2	R^3	R^4
a	H	H	H	H
b	Me	H	H	H
c	Me	H	Me	H
d	Me	Me	Me	H
e	Me	Me	Me	Me
f	H	H	- benzo-	

These products were isolated in over 90% yield by radial chromatography and identified by spectral comparison with authentic materials.

Kinetics

The kinetics of the reaction between dibenzoyl peroxides **1** and the hydroquinones **2** was followed spectrophotometrically at $\lambda = 430$ nm (formation of quinones) and found to obey the second-order rate law, first order in each component. The reaction rates were monitored over a period of at least one halflife. In all cases good linearity ($r > 0.98$) was obtained when $1/[H_2Q]_0 - [Q]$ was plotted against time. The reproducibility of the rate constants obtained in this way was better than 5%.

The solvent effect on the reaction rate was investigated for the dibenzoyl peroxide (**1d**)/trimethylhydroquinone (**2d**) pair. The rate constants over a wide range of solvent polarity, i.e. in four aprotic and three protic solvents, are shown in Table 1. Although the reaction rates were faster in protic than in aprotic solvents, the effects were small. This is clearly evident in the plots of $\ln k_2$ [M^{-1} s^{-1}] versus the dielectric constant D, which gave straight lines ($r > 0.99$) with slopes of 0.024 for aprotic and 0.006 for protic solvents.

Table 1. Solvent effect on the rate constants for the reaction between dibenzoyl peroxide (**1d**) and hydroquinone (**2d**)

Solvent[a]	Dielectric constant (D)	k_2 [10^{-3} M^{-1} s^{-1}][b]
Dioxane	2.21	2.80
Tetrahydrofuran	7.58	3.15
Acetone	20.7	4.49
Acetonitrile	36.0	6.29
Acetic acid	6.10	17.0
2-Propanol	18.3	18.5
Methanol	32.6	20.1
Chloroform/ethanol (1:1)	4.80/24.3	47.2

[a] Freshly distilled under nitrogen and purged with argon before use. — [b] Error ca. 5%, run at room temperature.

To probe substituent effects, the reaction rates of the six substituted dibenzoyl peroxides **1a**−**f**, which cover a wide range of Hammett substituent constants (σ), and the six hydroquinones **2a**−**f** were determined. The reaction rate was enhanced by electron-withdrawing substituents on the dibenzoyl peroxide. A satisfactory Hammett correlation (r = 0.969 to 0.990) with $\rho = +1.8 \pm 0.2$ was obtained by plotting $\ln k_X/k_H$ versus the σ substituent constants. The rate constants are listed in Table 2.

The dependence of the reaction rate on the hydroquinone oxidation potentials is demonstrated by the linear ($r > 0.981$) plots of $\log k_2$ [M^{-1} s^{-1}] versus $E^0(HQ^{\cdot}/H_2Q)$ [V] for each dibenzoyl peroxide with slopes of ca. 17 eV^{-1}. The reaction of bis(p-chlorobenzoyl) peroxide (**1c**) is ca. 1300 times faster with naphthohydroquinone (**2f**) than with hydroquinone (**2a**). Thus, as expected, the lower the oxidation potential of the hydroquinone, the faster the reduction of the peroxide.

The above rate data were processed by the Marcus equation (2) to determine the hitherto unknown reduction potentials of the substituted dibenzoyl peroxides, in which $\Delta G^{\neq}$ is the free energy of activation, $\Delta G^{0'}$ the standard free energy of reaction, and λ the energy parameter which describes the energy required for solvent and bond reorganization of the initially formed collision complex in the ET step. The $\Delta G^{\neq}$ term for the redox reaction is calculated by the Eyring equation (3), with $\kappa = 1$ and the frequency factor $Z = 10^{11}$ s^{-1}.

$$\Delta G^{\neq}\,[\mathrm{kcal\,mol^{-1}}] = \frac{\lambda}{4}\left(1 + \frac{\Delta G^{0\prime}}{\lambda}\right)^2 \qquad (2)$$

$$k_2[\mathrm{M^{-1}s^{-1}}] = \kappa Z \exp\left(\frac{\Delta G^{\neq}}{RT}\right) \qquad (3)$$

The $\Delta G^{0\prime}$ term is evaluated according to Eq. (4), in which ($E^0_\mathrm{D} - E^0_\mathrm{A}$) describes the potential difference in the rate-limiting step of the redox reaction. For the one-electron oxidation potential of the donor E^0_D = $E^0(\mathrm{HQ^{\bullet}/H_2Q})$ was chosen, because the potential for the formation of the radical cation $E^0(\mathrm{H_2Q^{+\bullet}/H_2Q})$ is not available. This approximation requires that the O–H bond of $\mathrm{H_2Q^{+\bullet}}$ is broken in the transition state, a fact that is well documented in ET chemistry[22a]. Consequently, the semiquinone radical ($\mathrm{HQ^{\bullet}}$) becomes the first intermediate of the redox reaction. The one-electron reduction potential of the acceptor E^0_A = $E^0(\mathrm{ROOR/RO^{\bullet}RO^-})$ is the potential of the dibenzoyl peroxide. W_el represents the electrostatic correction term given by Eq. (5) and is equal to -2.3 kcal mol^{-1}, when $Z_1 = Z_2 = 0$, $D = 36$ for acetonitrile, and $r_{12} = 400$ pm.

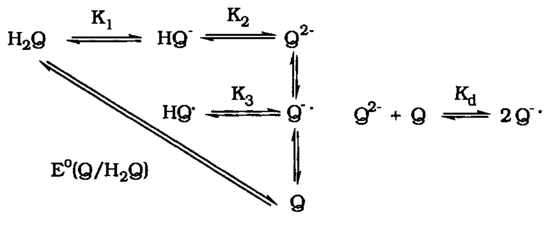
$$\Delta G^{0\prime}\,[\mathrm{kcal\,mol^{-1}}] = 23.06(E^0_\mathrm{D} - E^0_\mathrm{A}) + W_\mathrm{el} \qquad (4)$$

$$W_\mathrm{el}\,[\mathrm{kcal\,mol^{-1}}] = \frac{3.32 \times 10^{-8}}{D r_{12}}(Z_1 - Z_2 - 1) \qquad (5)$$

The one-electron oxidation potentials of the hydroquinones $E^0(\mathrm{HQ^{\bullet}/H_2Q})$ were estimated from the known[21] $E^0(\mathrm{Q/H_2Q})$ values by the thermodynamic cycle[22] in Scheme 1 according to Eq. (6) and are listed in Table 2. The unknown one-electron reduction potentials $E^0(\mathrm{ROOR/RO^{\bullet}RO^-})$ and the λ parameters were computed for each diaroyl peroxide according to the Marcus equation [Eq. (2)] by a nonlinear regression analysis and are also given in Table 2. Well-correlating plots with residual square sums in the range of 0.090 ± 0.065 were obtained in all cases. The λ values were found to be 17 ± 3 kcal mol^{-1}.

The reduction potentials of the diaroyl peroxides fall in a range of 47 mV for bis(*p*-methoxybenzoyl) peroxide (**1f**) and 150 mV for bis(*p*-nitrobenzoyl) peroxide (**1a**), which display that the reduction of these peroxides is facilitated by electron-withdrawing substituents. In fact, an exellent linear correlation ($r = 0.996$) was obtained for a plot of $E^0(\mathrm{ROOR/RO^{\bullet}RO^-})$ versus Hammett substituent constants (σ) with a slope of 100 mV per σ unit.

Scheme 1. Thermodynamic cycle for the calculation of $E^0(\mathrm{HQ^{\bullet}/H_2Q})$



$$E^0(\mathrm{HQ^{\bullet}/H_2Q})\,[\mathrm{V}] = E^0(\mathrm{Q/H_2Q}) + \frac{2.3\,RT}{2\,n\,F}\,(\mathrm{p}K_1 + \mathrm{p}K_2 - 2\mathrm{p}K_3 + \mathrm{p}K_\mathrm{d}) \qquad \text{(eq. 6)}$$

Discussion

The hydroquinones **2** are well-suited electron donors for the reduction of dibenzoyl peroxides **1** because this redox reaction leads exclusively to the corresponding benzoic acids **3** and quinones **4**. No side-products are formed, as it is the case with some other reagents, e.g. phenols[5] or methoxybenzenes[6]. Although one cannot distinguish rigorously between nucleophilic displacement ($\mathrm{S_N2}$) and electron transfer (ET) mechanism by means of product analysis alone, we consider the electron transfer mechanism of Scheme 2 plausible.

The small but consistent enhancement of the reaction rate with solvent polarity, measured in terms of the dielectric constant suggests that polar species are produced in the transition state, which are stabilized in polar solvents. The increase of the reaction rate in protic compared to aprotic solvents is presumably due to the more facile deprotonation of the strongly acidic hydroquinone radical cation ($\mathrm{H_2Q^{+\bullet}}$).

Significant is the pronounced substituent effect on the reaction rate for both the dibenzoyl peroxides and hydroquinones. Thus, electron-withdrawing substituents on the

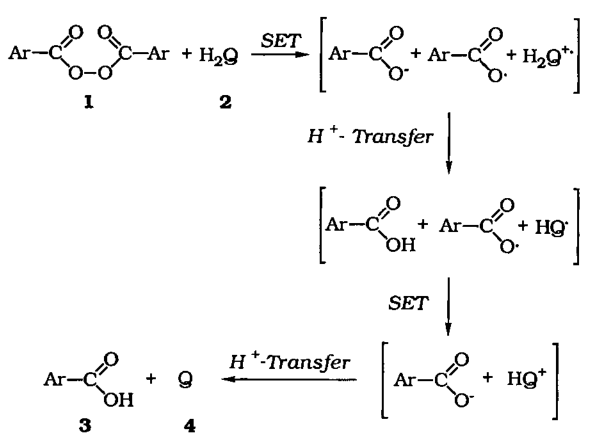
Table 2. Rate constants[a] for the reaction of dibenzoyl peroxides **1a–f** and hydroquinones **2a–f** in acetonitrile at 25 °C and reorganization energies λ and one-electron reduction potentials $E^0(\mathrm{ROOR/RO^{\bullet}RO^-})$ for the dibenzoyl peroxides, calculated according to the Marcus theory

$E^0(\mathrm{HQ^{\bullet}/H_2Q})$ [V][b]	**2a** 1.06	**2b** 1.01	**2c** 0.973	**2d** 0.925	**2e** 0.896	**2f** 0.874[c]	λ[d] [kcal mol^{-1}]	$E^0(\mathrm{ROOR/RO^{\bullet}RO^-})$[d] [mV]
1a	1.34	11.4	82.9	290	815	–[e]	15 ± 4	150 ± 11
1b	0.380	2.59	10.8	59.8	158	394	18 ± 1	106 ± 2
1c	0.156	1.28	5.66	37.7	92.8	204	17 ± 3	90 ± 6
1d	0.066	0.495	2.72	9.35	29.2	40.4	23 ± 7	69 ± 31
1e	–[f]	0.150	1.66	4.85	26.6	51.7	15 ± 8	54 ± 34
1f	–[f]	0.109	1.10	4.22	20.9	40.0	15 ± 7	47 ± 33

[a] Mean values of k_2 [10^{-3} M^{-1} s^{-1}] from up to four independent measurements, error ca. 5%. – [b] Evaluated according to Scheme 1 and Eq. (6). – [c] Estimated from the corresponding two-electron oxidation potentials. – [d] Error range corresponds to the asymptotic 95% confidence interval. – [e] Rate constant not measurable because of overlap with the dibenzoyl peroxide (**1a**) absorbance. – [f] Reaction too slow, halflife estimated to be $t_{1/2} > 400$ h.

dibenzoyl peroxides and electron-donating substituents on the hydroquinones enhance the reaction rates, as could be verified by well-correlating semilogarithmic plots of the rate constants against the Hammett substituent constants (σ). The positive reaction constant of $\varrho = +1.8 \pm 0.2$ indicates accumulation of negative charge at the dibenzoyl peroxide in the rate-limiting reaction step; the rather large value of ϱ reveals the high susceptibility of the reaction towards substituent effects.

Scheme 2. Electron transfer mechanism of the reduction of dibenzoyl peroxides **1** by hydroquinones **2**



The measured rate constants k_2 gave good semilogarithmic plots versus the calculated hydroquinone one-electron oxidation potentials $E^0(HQ^\bullet/H_2Q)$ with a slope of ca. 17 eV^{-1}. This value represents the limiting slope of the Marcus parabola in the endergonic region for ET reactions of quite low reorganization energies (λ). The nonlinear regression analysis according to the Marcus equation [Eq. (2)–(5)] afforded in all cases well-fitting correlations, which is in accord with the assumed ET reaction. The one-electron reduction potentials of the various substituted dibenzoyl peroxides $E^0(ROOR/RO^\bullet\ RO^-)$ were estimated to fall in the range of 47 to 150 mV. These values compare well with the thermodynamically calculated value of 0.0 V in acetonitrile[16] and polarographically measured 0.1 V in benzene/methanol[17] for unsubstituted dibenzoyl peroxide (**1d**). As expected, the reduction potential increases with increasing electron demand at the dibenzoyl peroxide, which is convincingly demonstrated by an excellent ($r = 0.996$) Hammett plot of $E^0(ROOR/RO^\bullet\ RO^-)$ versus σ.

The low reduction potentials estimated for the dibenzoyl peroxides imply an endergonic rate-limiting electron transfer step, which is analogous to other irreversible redox reactions, for example, alkyl halides[14]. The driving force for the electron transfer derives from the irreversible dissociation of the peroxide bond, which results in removing the initially formed radical anion from the equilibrium. This is comparable to reactions in which high-energy intermediates are formed, like for example in the electrophilic aromatic nitration[23]. The so called Wheland intermediate $Ar^+(H)NO_2$ is generated in an endergonic electron transfer step, which further reacts by an irreversible proton transfer to the nitro compound.

The reorganization energies (λ), estimated for the redox reactions between the dibenzoyl peroxides and hydroquinones, fall in the range of 17 ± 3 kcal mol^{-1} and are comparatively low for a dissociative outer-sphere electron transfer process. Since outer-sphere ET processes are rare for organic reactions and examples are known[11], which obey Marcus-theory, we postulate that the dibenzoyl peroxide/hydroquinone redox reaction investigated here involves inner-sphere electron transfer. Much lower reorganization energies should be expected for inner-sphere compared to outer-sphere processes[11]. Because of the greater polar character of the inner-sphere transition state, stronger electronic interactions are expected. For example, in the case of the reduction of dioxygen ($O_2/O_2^{-\bullet}$) by various organometallic compounds, greatly varying values for the reorganization parameter (λ) were obtained experimentally[24].

The choice of $E^0(HQ^\bullet/H_2Q)$ as the donor oxidation potential may influence the λ value; however, for a series of comparable hydroquinones a constant correction should apply. Presumably, the actual $E^0(H_2Q^{+\bullet}/H_2Q)$ potentials will be higher than the presently employed $E^0(HQ^\bullet/H_2Q)$ potentials, so that the addition of a constant correction term should lead to higher $E^0(ROOR\ RO^\bullet\ RO^-)$ reduction potentials, but the λ parameter should not change. On the other hand the addition of a nonconstant correction term would flatten the Marcus parabola with the effect of affording higher λ values.

In conclusion, by employing the Marcus theory, for the first time reorganization energies and reduction potentials of a series of dibenzoyl peroxides have been made available from kinetic data of their irreversible redox reaction with hydroquinones. The well-behaved correlation (Hammett plot) between the observed reduction potentials of the dibenzoyl peroxides and their substituents, i.e. electron-accepting groups facilitate reduction ($\varrho = -1.8 \pm 0.2$), confirm that negative charge builds up on the peroxide in the transition state for this ET reaction. The low λ value suggests, that an inner-sphere mechanism operates in this ET reaction.

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Experimental

Materials: The dibenzoyl peroxides **1** were prepared from the corresponding acyl chlorides and sodium peroxide[25] and recrystallized from $CHCl_3$/MeOH. Their purity (>99%) was determined by iodometry[26]. 2,5-Dimethyl-[27], duro-[28], and naphthohydroquinone[29] were prepared from the corresponding quinones by reduction with sodium dithionite or with sodium tetrahydridoborate. 2,5-Dimethylquinone was prepared from 2,5-dimethylphenol by oxidation with 85% hydrogen peroxide[30]. Acetonitrile, used for the kinetic measurements, was refluxed over calcium hydride under nitrogen for 3 h, distilled, stored under argon and purged vigorously before use with argon for 3 min.

Product Studies: For the identification of the products, the benzoic acids **3** and quinones **4** were isolated from preparative runs (0.500 mmol of dibenzoyl peroxides, 0.600 mmol of hydroquinones, 20°C, acetonitrile) by radial chromatography (silica gel 60, 1-mm layer thickness; petroleum ether, b.p. 30–50°C) in yields greater than 90%. Comparison of the melting points and the ^{1}H-NMR spectra with authentic samples established the identity of the isolated products. No other products could be detected by TLC or ^{1}H NMR. The quantitative analysis of the products was carried out by ^{1}H-NMR spectroscopy directly on the crude reaction mixture in [D$_3$]acetonitrile, with hexamethyldisiloxane as internal standard.

Kinetics: The rate measurements of the dibenzoyl peroxide/hydroquinone reaction were carried out under argon in thermostated 1-cm cuvettes at 25°C and by monitoring the appearance of the quinone absorbance at $\lambda_{max} > 400$ nm with a Hitachi U 3200 spectrophotometer. The kinetics were investigated under second-order conditions, i.e. equimolar in both dibenzoyl peroxide and hydroquinone. To 2 ml of saturated dibenzoyl peroxide solution in acetonitrile was added 1 ml of hydroquinone solution in acetonitrile, so that the concentration of both components were equal in the final mixture. To achieve better mixing, the hydroquinone solution was added by means of a syringe. The absorbance (A) of the quinone product was read and converted into concentration units ([Q]) by using Beer's law ($[Q] = A/d \cdot \varepsilon; d = 1$ cm). The extinction coefficients (ε) of the quinones were taken from literature[31], except for naphthoquinone ($\varepsilon = 49.3$ M^{-1} cm^{-1} at $\lambda = 412$ nm), which was determined experimentally. Plots of $([H_2Q]_0 - [Q])^{-1}$ versus time exhibited good linearity ($r > 0.98$). The slope gave the rate constant k_2 [M^{-1} s^{-1}] and the intercept the $[H_2Q]_0^{-1}$ value.

Computation of the λ Values and the Reduction Potentials of the Dibenzoyl Peroxides: Nonlinear regression analysis according to the Marcus theory (Eq. (2) and Eq. (4)) were carried out with a Siemens 7.860 computer, kindly made available by the Computer Center of the University of Würzburg. A program was used which allowed fitting the data according to the Marquardt method.

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