Mechanism of Photosensitized Generation of Singlet Oxygen during Oxygen Quenching of Triplet States and the General Dependence of the Rate Constants and Efficiencies of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ Formation on Sensitizer Triplet State Energy and Oxidation Potential

Claude Schweitzer,† Zahra Mehrdad, Astrid Noll, Erich-Walter Grabner, and Reinhard Schmidt*

Institut für Physikalische und Theoretische Chemie, Johann Wolfgang Goethe-Universität, Marie-Curie-Strasse 11, D60439 Frankfurt am Main, Germany

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Rate constants of photosensitized generation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ have been determined for a series of $\pi\pi^*$ triplet sensitizers with strongly varying oxidation potential (E_{ox}), triplet energy (E_T), and molecular structure, in CCl_4. We demonstrate that one common dependence on E_{ox} and E_T successfully describes these rate constants for the molecules studied here and also for all previously investigated $\pi\pi^*$ sensitizers, independently of molecular structure or any other parameter. Photosensitized singlet oxygen generation during O_2 quenching of $\pi\pi^*$ triplet states can be generally described by a mechanism involving the successive formation of excited noncharge transfer (nCT) encounter complexes and partial charge transfer (pCT) exciplexes of singlet and triplet multiplicity $^{1,3}(T_1{}^3\Sigma)$, following interaction of $O_2(^3\Sigma_g^-)$ with the triplet excited sensitizer. Both $^{1,3}(T_1{}^3\Sigma)$ nCT and pCT complexes decay by internal conversion (ic) to yield $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ and the sensitizer ground state. ic is the rate-limiting step in the nCT channel, whereas exciplex formation is rate determining in the pCT channel. Rotation of the O_2 molecule within the solvent cage of $^{1,3}(T_1{}^3\Sigma)$ nCT complexes is fast enough to allow for a completely established intersystem crossing (isc) equilibrium, whereas significant noncovalent binding interactions slow rotation and inhibit isc between $^1(T_1{}^3\Sigma)$ and $^3(T_1{}^3\Sigma)$ pCT complexes. Upon the basis of this mechanism, we propose a semiempirical relationship that can be generally used to estimate rate constants and efficiencies of photosensitized singlet oxygen generation during O_2 quenching of $\pi\pi^*$ triplet states in CCl_4. The data set includes 127 rate constants for derivatives of naphthalene, biphenyl, fluorene, several ketones, fullerenes, porphyrins and metalloporphyrins, and other homocyclic and heterocyclic aromatics of variable molecular structure and size. It is suggested that the general relationship presented here can be used for the optimization of the singlet oxygen photosensitization ability of many molecules, including those used in biological and medical applications, such as the photodynamic therapy of cancer.

Introduction

The photosensitized production of the lowest excited singlet states $^1\Sigma_g^+$ and $^1\Delta_g$ of O_2 during oxygen quenching of excited triplet (T_1) states is a process of major importance to the chemical, biological, and medical sciences. The first excited state, $O_2(^1\Delta_g)$, which is commonly being referred to as singlet oxygen, is an extremely reactive and highly cytotoxic species and is responsible for natural photodegradation processes and photocarcinogenesis, but also has significant applications, for example in organic synthesis and in the photodynamic therapy of cancer. In solution, the second excited singlet state, $O_2(^1\Sigma_g^+)$, which can be formed in competition to $O_2(^1\Delta_g)$, is very rapidly and quantitatively deactivated to the long-lived $O_2(^1\Delta_g)$ species.[1,2] Since the pioneering work of Gijzeman et al.,[3] mechanistic studies have endeavored to establish a relationship between the physical properties of a sensitizer and the rate constants and efficiencies of singlet oxygen formation during O_2 quenching of T_1 states. Significant advances have been made on the basis of correlations with the sensitizer triplet energy E_T and oxidation potential E_{ox}, but despite sustained efforts carried out over the past 30 years and a huge amount of experimental data available,[4,5] a general quantitative relationship is still lacking. We will propose here, for the first time, a general relationship that describes how variations of E_T *and* E_{ox} influence the rate constants of formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and ground-state oxygen $O_2(^3\Sigma_g^-)$ during O_2 quenching of T_1 states in CCl_4.

This relationship relies upon the photosensitization mechanism displayed in Figure 1, which is based on a scheme originally proposed by Gijzeman et al.,[3] and later modified by Wilkinson and co-workers[6−15] and ourselves.[16−18] Figure 1 also features a graphical representation of the conclusions from recent discussions of the structure of intermediate complexes involved in the photosensitized generation of singlet oxygen.[18−21]

The scheme in Figure 1 infers that T_1-excited sensitizer and $O_2(^3\Sigma_g^-)$ form, with diffusion-controlled rate constant k_{diff} (2.7×10^{10} M^{-1} s^{-1} in CCl_4) excited $^m(T_1{}^3\Sigma)$ encounter complexes with multiplicities $m = 1$, 3 and 5, which either dissociate again with rate constant k_{-diff} (assumed to be $k_{-diff} = k_{diff}/M^{-1} = 2.7 \times 10^{10}$ s^{-1}, as previously done by Gijzeman et al.,[3] Wilkinson

* To whom correspondence should be addressed. E-mail: R.Schmidt@chemie.uni-frankfurt.de.

† Present address: Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada.

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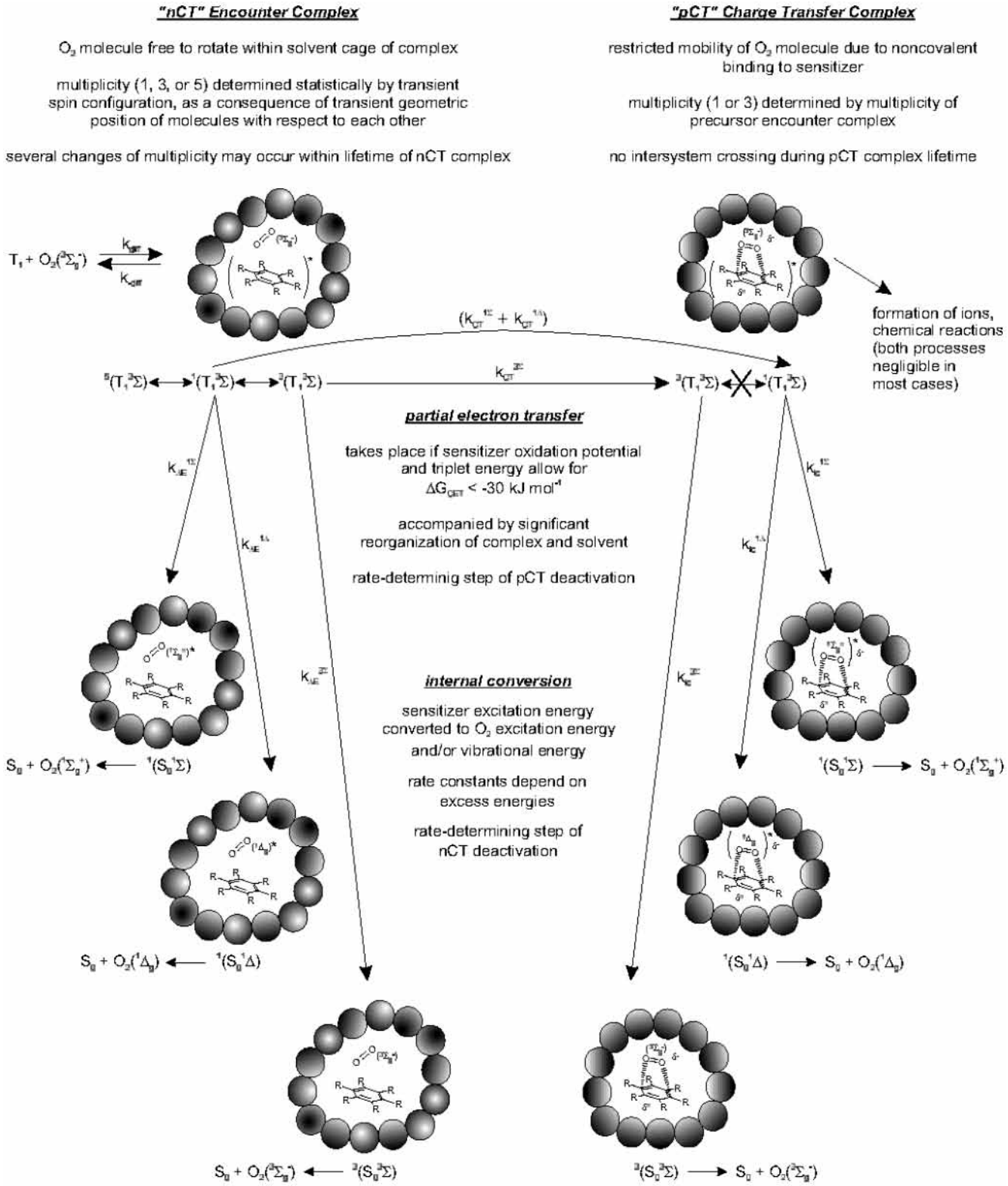

Figure 1. Mechanism of photosensitized generation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ during O_2 quenching of triplet states. The scheme shows the different noncharge transfer and partial charge transfer complexes in their solvent cage. The mechanism applies generally to $\pi\pi^*$ excited aromatic hydrocarbons, including five- and six-membered rings, with and without heteroatoms or metal centers, as we demonstrate here.

et al.,[6−15] and ourselves)[16−21] or yield the quenching products with overall rate constant k_D

$$k_D = k_{-diff} k_T^Q / (k_{diff} - k_T^Q) \quad (1)$$

where k_T^Q is the experimental quenching rate constant. $k_D = k_{\Delta E}{}^{1\Sigma} + k_{\Delta E}{}^{1\Delta} + k_{\Delta E}{}^{3\Sigma} + k_{CT}{}^{1\Sigma} + k_{CT}{}^{1\Delta} + k_{CT}{}^{3\Sigma}$ accounts for the internal conversion (ic) of excited $^{1,3}(T_1{}^3\Sigma)$ encounter complexes with no charge-transfer character (nCT) to the lower-lying nCT complexes $^1(S_0{}^1\Sigma)$, $^1(S_0{}^1\Delta)$, and $^3(S_0{}^3\Sigma)$ (which occurs with rate constants $k_{\Delta E}{}^{1\Sigma}$, $k_{\Delta E}{}^{1\Delta}$, and $k_{\Delta E}{}^{3\Sigma}$, respectively), as well as for the formation of $^1(T_1{}^3\Sigma)$ and $^3(T_1{}^3\Sigma)$ partial charge transfer (pCT) complexes, which originates from $^{1,3}(T_1{}^3\Sigma)$ nCT complexes, with rate constants ($k_{CT}{}^{1\Sigma} + k_{CT}{}^{1\Delta}$) and $k_{CT}{}^{3\Sigma}$, respec-

tively. Excited pCT complexes decay by rapid ic ($k_{ic}^{1\Sigma}$, $k_{ic}^{1\Delta}$, or $k_{ic}^{3\Sigma}$) to lower-lying pCT complexes, and all species involving the sensitizer ground state (S_0) dissociate to give S_0 and $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, or $O_2(^3\Sigma_g^-)$.

In the original work of Gijzeman et al.,[3] experimental O_2 quenching rate constants for a series of sensitizers in several solvents were found to be generally smaller than $1/9k_{diff}$ and to correlate with the sensitizer triplet energy. On the basis of these results, it was suggested that O_2 quenching of excited triplets exclusively proceeds via singlet encounter complexes, and that no isc takes place between the complexes of different multiplicity. However, later studies provided clear evidence for k_T^Q values in excess of $1/9k_{diff}$[6,17,22−28] and even of $4/9k_{diff}$,[29−31] thus showing that complexes of singlet, triplet, and quintet multiplicity can significantly contribute to the overall mechanism. Moreover, a large number of studies showed that, for easily oxidizable molecules, rate constants correlate with the ease of oxidation of the sensitizer, which means that O_2 quenching of T_1 states proceeds, at least partially, via exciplexes.[7−21,23,31,32] However, the dependence of experimental data on redox properties was found to be significantly weaker than expected for a complete electron transfer, and all authors largely agreed that only a partial transfer of charge takes place. Different estimates have been proposed for the charge-transfer character (δ) of the involved exciplexes. For example, a linear interpretation of experimental data for a series of biphenyl derivatives yielded a decrease of δ with increasing solvent polarity, from 17% in cyclohexane to 12.5% in acetonitrile,[12] whereas a parabolic Marcus-type model led significantly larger values, and to an increase of δ with increasing solvent polarity, from 43% in CCl_4 to 58% in acetonitrile, for the same molecules.[20] In addition to quenching rate constants, a significant number of studies have also provided data on the efficiency S_Δ of singlet oxygen formation during O_2 quenching of T_1, which represents the sum of the efficiencies a of formation of $O_2(^1\Sigma_g^+)$ and $b = S_\Delta - a$ of directly formed $O_2(^1\Delta_g)$.[7−21,28,31,32] This allows the calculation of the overall rate constants for T_1 deactivation via the triplet channel, $k_T^{3\Sigma}$, and via the singlet channel, $(k_T^{1\Sigma} + k_T^{1\Delta})$, where $k_T^{1\Sigma}$ and $k_T^{1\Delta}$ are the rate constants of $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ formation, respectively. Both $k_T^{3\Sigma}$ and $(k_T^{1\Sigma} + k_T^{1\Delta})$ correlate with sensitizer E_{ox}, but the dependence was found to be weaker for $(k_T^{1\Sigma} + k_T^{1\Delta})$ in most cases. It was thus concluded that at least the formation of $O_2(^1\Delta_g)$ can occur from both encounter complexes and charge-transfer complexes.[12−15,31,32]

The recent development of novel spectroscopic methods for the time-resolved observation of $O_2(^1\Sigma_g^+)$ allowed us to determine a and $b = (S_\Delta - a)$ with sufficient accuracy and, thus, to separate k_D into the single rate constants of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ formation, which are given by eqs 2−4:[1,33]

$$k_T^{1\Sigma} = ak_D \tag{2}$$

$$k_T^{1\Delta} = (S_\Delta - a)k_D \tag{3}$$

$$k_T^{3\Sigma} = (1 - S_\Delta)k_D \tag{4}$$

The first investigation with this technique showed that, for a series of sensitizers with strongly varying E_T, the multiplicity-normalized rate constants k_T^P/m (i.e., $k_T^{1\Sigma}/1$, $k_T^{1\Delta}/1$, and $k_T^{3\Sigma}/3$) depend on the excess energy ΔE for formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ from $^{1,3}(T_1{}^3\Sigma)$ encounter complexes, which is given by $E_T - 157$, $E_T - 94$, and E_T, respectively (in kJ mol^{-1}).[34] This is in agreement with the results of Gijzeman et al.,[3] and also with the early theoretical study of Kawaoka et al.,[35] where the rate constants for the ic from excited $^{1,3,5}(T_1{}^3\Sigma)$ complexes to the lower-lying nCT complexes $^1(S_0{}^1\Sigma)$, $^1(S_0{}^1\Delta)$, and $^3(S_0{}^3\Sigma)$ (represented by k_{ic} in eq 5) were expressed as a function of the electronic coupling matrix element between initial and final states, β, and of the Franck−Condon factors $F(\Delta E)$ and the density of final states, $\rho(\Delta E)$ which both depend on ΔE

$$k_{ic} = (4\pi^2/h)\,\rho(\Delta E)\,F(\Delta E)\,\beta^2 \tag{5}$$

However, k_T^P/m data for sensitizers with low oxidation potentials deviate significantly from this correlation, and it was found that, in this case, the E_{ox} dependence of multiplicity-normalized rate constants for formation of all three O_2 product states becomes more important than the correlation with ΔE.[16−18] It was thus suggested that, in general, the multiplicity-normalized rate constants for formation of each O_2 product state are additively composed of a nCT component $k_{\Delta E}^P/m$ and a pCT component k_{CT}^P/m (eqs 6−8), which means that formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ proceeds via both encounter complexes and exciplexes (Figure 1)[16−18]

$$k_T^{1\Sigma}/1 = k_{CT}^{1\Sigma}/1 + k_{\Delta E}^{1\Sigma}/1 \tag{6}$$

$$k_T^{1\Delta}/1 = k_{CT}^{1\Delta}/1 + k_{\Delta E}^{1\Delta}/1 \tag{7}$$

$$k_T^{3\Sigma}/3 = k_{CT}^{3\Sigma}/3 + k_{\Delta E}^{3\Sigma}/3 \tag{8}$$

The study of a series of sensitizers with strongly varying E_T suggested that the rate constants for the nCT pathway are described by the empirical polynomial of eq 9[34]

$$\log(k_{\Delta E}^P/m) = 9.05 + 9 \times 10^{-3}\,\Delta E - 1.15 \times 10^{-4}\,\Delta E^2 + 1.15 \times 10^{-7}\,\Delta E^3 + 9.1 \times 10^{-11}\Delta E^4 \tag{9}$$

This assumption was also supported by later E_{ox}-dependent studies, which revealed that the k_T^P/m values for sensitizers with the highest oxidation potentials, i.e., where CT effects are unlikely, are also described by eq 9.[16−18] Hence, it seems to be established that eq 9 reflects the ΔE-dependence of the internal conversion of encounter complexes $^{1,3}(T_1{}^3\Sigma)$ without CT stabilization. However, this dependence is weaker than predicted by eq 5 using $F'(\Delta E) = \rho(\Delta E)F(\Delta E)$ calculated according to a relationship established by Siebrand[36−38] for the ic between deep potential minima of strongly bound aromatic molecules.[34] It is thus suggested that nCT $^{1,3,5}(T_1{}^3\Sigma)$ complexes involve weak binding interactions and shallow potential minima.[34] Finally, the common ΔE dependence of all $\log(k_{\Delta E}^P/m)$ data also implies that the matrix elements for ic of all $^{1,3}(T_1{}^3\Sigma)$ complexes are the same and that there is a fully established isc equilibrium between nCT encounter complexes.[34]

Using eqs 6−9 to estimate the nCT and pCT contributions to k_T^P/m, investigations of several series of sensitizers with strongly varying E_{ox} and constant E_T[16−18] showed that k_{CT}^P/m depends on the free energy ΔG_{CET} for complete electron transfer from the T_1-excited sensitizer to O_2, which is given by the Rehm−Weller equation[39,40]

$$\Delta G_{CET} = F(E_{ox} - E_{red}) - E_T + C \tag{10}$$

where F is the Faraday constant and E_{red} is the reduction potential of molecular oxygen (−0.78 V vs SCE in acetonitrile).[41] The electrostatic interaction energy C has been neglected in all previous studies and in the present because all data were

determined in the same solvent.[16−18] These studies revealed that empirical linear relationships of the form of eq 11 can be used to describe the dependence of k_{CT}^P/m on ΔG_{CET}

$$\log(k_{CT}^P/m) = \log(c^P/m) + c_1 - c_2\,\Delta G_{CET} \qquad (11)$$

c_1 and c_2 are positive empirical constants which are characteristic for each series.[16−18] Three studies clearly established that different correlations exist for each O_2 product state, which means that the three channels have a different statistical weight. This is expressed by the constant c^P in eq 11, which was determined to be $c^{1\Sigma} = 0.67$, $c^{1\Delta} = 0.33$, and $c^{3\Sigma} = 3.00$, for formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$, respectively.[16−18] These weight factors imply that the graduation $k_{CT}^{3\Sigma}/3 > k_{CT}^{1\Sigma} > k_{CT}^{1\Delta}$ holds true. Thus, the charge-transfer induced formation of singlet oxygen is not governed by an energy gap law, because in this case the graduation $k_{CT}^{1\Sigma} > k_{CT}^{1\Delta} > k_{CT}^{3\Sigma}/3$ would result.[16−18] Therefore, the decay of excited pCT exciplexes to lower-lying pCT complexes (labeled $k_{ic}^{1\Sigma}$, $k_{ic}^{1\Delta}$, and $k_{ic}^{3\Sigma}$ in Figure 1) cannot be rate determining. This was unexpected, because previous temperature-dependent measurements of McLean and Rodgers[29,42,43] showed that O_2 quenching of several triplet states is associated with slightly negative activation enthalpies ($\Delta H^{\#}$) of about -5 kJ mol^{-1} in the high temperature region, a behavior which these authors explained by the formation of a preequilibrium at the level of the exciplex, which would mean that exciplex decay has to be rate determining. However, later studies of Rau et al. showed that negative activation enthalpies do not necessarily imply preequilibrium conditions.[44,45] The position of the transition state on the hypersurface of the reaction coordinate is defined by the maximum of the activation free energy $\Delta G^{\#}$. At this point of the reaction coordinate, $\Delta H^{\#} = \Delta G^{\#} + T\Delta S^{\#}$ can be negative, if the corresponding activation entropy $\Delta S^{\#}$ is negative enough. Thus, an elementary reaction may exhibit a negative enthalpy of activation too. This has been demonstrated by Rau et al. for photoinduced electron transfer from excited **[**tris(2,2′-bipyridine)ruthenium(II)**]**$^{2+}$ to some anthraquinones with small positive or negative Gibbs energies of reaction.[45] Thus, the formation of $^{1,3}(T_1{}^3\Sigma)$ exciplexes from $^{1,3}(T_1{}^3\Sigma)$ encounter complexes could well be rate-determining. Finally, the unexpected graduation of rate constants reported for the pCT channel in several papers also implies that there is no isc at the level of the pCT complexes, because isc would establish an energy-gap dependent behavior.[16−18] This was also unexpected, because, in the absence of experimental evidence, all previous investigations assumed that isc takes place at the level of both nCT encounter complexes and pCT exciplexes.[11−13,31]

Mehrdad et al.[18] explained this behavior by a mechanism where isc in the nCT complexes is coupled to the rotation of the O_2 molecule (which is estimated to be significantly faster than the decay of nCT complexes), whereas in the pCT complexes, rotation (and thus isc) is restricted by significant noncovalent binding of the O_2 molecule to the aromatic ring of a $\pi\pi^*$ sensitizer. This is also in agreement with the previously suggested oriented supra−supra structure of the pCT complexes,[19−21] which is thought to be similar to that formed during pCT induced deactivation of $O_2(^1\Delta_g)$ by benzene.[46] The limiting structures of nCT and pCT complexes are also represented in Figure 1.

Additionally, information on the energetics of structural changes associated with the charge-transfer process have been obtained from a Marcus-type interpretation of experimental data, from which reorganization energies (λ) can be calculated.[47] These can be separated into an intramolecular contribution (λ_i) and a solvent dependent part (λ_o), if the amount of charge transferred (i.e., δ) is known.[48] Estimates of δ according to a Marcus-type model led to λ_i values of the order of 30 kJ mol^{-1} for a series of naphthalene and biphenyl derivatives and to a strong increase of λ_o with increasing solvent polarity, from 1.4 kJ mol^{-1} (CCl_4) to 60 kJ mol^{-1} (CH_3CN).[20]

Finally, it is important to know that all mechanistic conclusions described here apply exclusively to $\pi\pi^*$ excited triplets. Although the very vast majority of singlet oxygen sensitzers have a $\pi\pi^*$ triplet state configuration, it should be noted that nπ^* excited ketones exhibit a significantly different behavior, which has been previously discussed in detail.[21,49]

Hence, the mechanism of singlet oxygen photosensitization during O_2 quenching of triplet states seems to be well-established. However, two important points remained unclear in previous work: First, the E_{ox} values of the compounds studied in ref 34 were unknown, and hence, the influence of CT interactions could not be quantitatively understood in this investigation. Additionally, recent work has raised the question, to what extent $k_{\Delta E}^P/m$ is influenced by the molecular structure of the sensitizer.[18] To address these two issues, and to find out whether *one* dependence on ΔE *and* ΔG_{CET} describes the values of k_T^P/m in a general way and whether the mechanism described here can be generally applied to $\pi\pi^*$ excited triplets, we have now extended our study to a series of compounds with strongly varying molecular structure and determined the E_{ox} values of all previously investigated sensitizers.

Experimental Section

Carbon tetrachloride (Acros, 99+%, Al_2O_3) and phenalenone (Aldrich, 97%, CH_2Cl_2/silica gel) were purified by column chromatography. Quinoxaline (Aldrich, 99%) was vacuum sublimed. Water-free acetonitrile (Merck, Selectipur), coumarin (ICN Biomedicals), chrysene (Aldrich, 95%), benzo[*h*]quinoline (Aldrich, 97%), pyrene-1-carboxaldehyde (Lancaster, 99%), dibenzo[a,c]anthracene (Aldrich, 97%), tetrachloro-p-benzoquinone (Janssen Chimica, 99%), tetraphenylporphine zinc (Aldrich), octaethylporphine zinc (Aldrich, 98%), fullerene C_{60} (Lancaster, 99+%), fullerene C_{70} (Lancaster, 98%), tetraphenylporphine (Aldrich, 99%), phenazine (Aldrich, 98%), acridine (Aldrich, 97%), benzanthrone (Lancaster, 99+%), fluorenone (Aldirch, 98%), 2-acetonaphthone (Aldrich, 99%), 4-benzoylbiphenyl (Aldrich, 99%), triphenylene (Aldrich, 98%), and tetrabutylammoniumhexafluorophosphate (Aldrich, 98%) were used as received. Solutions for luminescence measurements were prepared and filled into sample cells in a glovebox under dry atmosphere to avoid the uptake of humidity in the investigation of $O_2(^1\Sigma_g^+)$. Irradiation was provided by a XeCl excimer laser (ATL Lasertechnik) at 308 nm. The $O_2(^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-)$ phosphorescence was recorded at 764 nm using a Hamamatsu PM R1464 photomultiplier, the $O_2(^1\Sigma_g^+ \rightarrow {}^1\Delta_g)$ fluorescence was detected at 1940 nm using a liquid N_2-cooled InAs diode (EG&G Judson J12-D) with a preamplifier (EG&G Judson PA7), and the $O_2(^1\Delta_g \rightarrow {}^3\Sigma_g^-)$ phosphorescence was recorded at 1275 nm using a cryogenic Ge diode (North Coast EO817P). Luminescence signals were digitized using a digital storage oscilloscope (Tektronix TDS210 or TDS3052). All signals were recorded at room temperature, in air-saturated solutions of dry CCl_4, in the absence and presence of 7 vol % benzene. The method used for the determination of the rate constants $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}$ of formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ has been previously described in detail.[1,33] All sensitizers were directly irradiated at 308 nm. A total of 16 laser shots were averaged for $O_2(^1\Sigma_g^+ \rightarrow {}^1\Delta_g)$ and $O_2(^1\Delta_g \rightarrow {}^3\Sigma_g^-)$ signals and

TABLE 1: Ionization Energies IE and Measured and Estimated Oxidation Potentials E_{ox}^{n}

compound	IE, eV	E_{ox}, V vs Ag/AgCl	E_{ox}, V vs SCE
octaethylporphine zinc	6.29[a]	1.04	0.95[g]
tetraphenylporphine zinc	6.23[a]	1.05[l]	0.96[h]
tetraphenylporphine	6.36[a]	1.12[l]	1.03[i]
9-bromoanthracene	7.53[a,c]	1.50	1.41
dibenzo[*a*,*h*]anthracene	7.45[a,b]	1.52	1.43
pyrene-1-carboxyaldehyde		1.54	1.45
chrysene	7.60[d]	1.65	1.56
acridine	7.87[a,b]	1.75	1.66
benzanthrone	8.00[e]	1.75	1.66
triphenylene	7.87[d]	1.80	1.71
fullerene C_{60}	7.60[f]	1.85[l]	1.76[j]
fullerene C_{70}	7.60[f]	1.85[l]	1.76[j]
benzo[*h*]quinoline	8.19[a,b]	1.90	1.81
phenalenone	8.20[a]	2.05	1.96
2-acetonaphthone	8.31[a]	2.10	2.01
phenazine	8.37[a]	2.10	2.01
fluorenone	8.34	2.20	2.11
4-benzoylbiphenyl		2.22	2.13
coumarin	8.72[e]	2.33	2.24
quinoxaline	9.01[d]	2.50[m]	2.41
duroquinone	9.17[a]	2.59[m]	2.50
4-methylbenzophenone	9.13[b]	2.60[k]	2.51
benzophenone	9.08[d]	2.85[k]	2.76
tetrachloro-*p*-benzoquinone	9.82[a]	2.95[m]	2.86

[a] Reference 54. [b] Reference 55. [c] Reference 56. [d] Reference 57. [e] Reference 58. [f] Reference 59. [g] Reference 60. [h] Reference 61. [i] Reference 62. [j] Reference 63. [k] Reference 21. [l] Measured vs SCE. [m] Estimated by the correlation $E_{ox} = 0.5602\ IE - 2.55$. [n] All E_{ox} values have been measured vs Ag/AgCl reference electrode unless otherwise noted. SCE values are obtained by subtracting 0.09 V from values measured vs Ag/AgCl.

at least 64 shots for $O_2(^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-)$ signals. Only energy-independent results are reported.

The values of E_{ox} listed in Table 1 were determined by cyclic voltammetry. They are interpreted as one-electron oxidations of the neutral organic molecules to the corresponding radical cations. This is supported by the peak currents of the oxidation waves being nearly equal to that of a reversible one-electron oxidation (e.g., of perylene) at the same concentration. The cyclic voltammograms were not reversible, because the reverse reduction peaks were found to be diminished or even absent. If a reverse peak was observed, e.g., for 2,7-dibromofluorene,[18] the separation of oxidation and reduction peaks amounted about 60 mV. It is assumed that the reversible one-electron transfer is followed by some irreversible chemical reaction of the radical cations. In such a so-called E_rC_i system (reversible electron transfer with consecutive irreversible chemical reaction), the peak potential depends on the rate constant k of the follow-up reaction shifting it to more negative values by about 30 mV per 10-fold increase of k with respect to the peak potential of a pure E_r system. Thus, accurate redox potentials cannot be evaluated. However, assuming that the variation of k does not exceed 3 orders of magnitude in the different systems with respect to the reversible E_r case at the voltage scan rates used, the E_{ox} values reported are considered as lower limits of the thermodynamic redox potentials with an uncertainty of 0.1 V. These values serve as means for the estimation of the extent of charge-transfer interactions in the triplet state quenching by O_2.

The cyclic voltammograms were obtained using the Bank POS 73 potentioscan. A three-electrode system was employed with a platinum disk as the working electrode, an Ag/AgCl reference electrode, and a platinum wire as the counter electrode. All measurements were carried out at room temperature, in deoxygenated solutions of water-free acetonitrile containing 10^{-3} M of the sensitizer and 0.1 M tetrabutylammoniumhexafluorophosphate as supporting electrolyte. The voltage scan was varied between 20 and 200 mV s^{-1}. The data listed refer to the scan rate of 50 mV s^{-1} throughout.

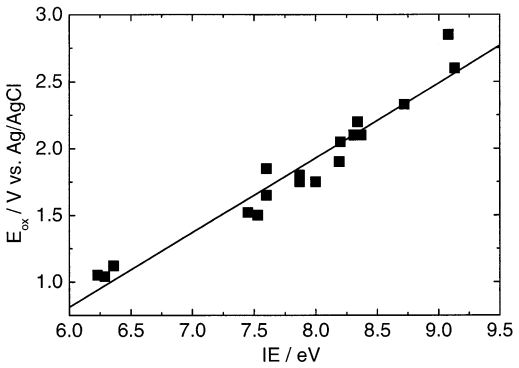

Figure 2. Correlation of E_{ox} vs IE. Data of Table 1. Solid line is given by $E_{ox} = 0.5602\ IE - 2.55$.

TABLE 2: Experimental Photophysical and Electrochemical Parameters for O_2 Quenching of T_1 States in CCl_4

sensitizer	T_1 yield	k_T^Q, $10^9\ M^{-1}\ s^{-1}$[c]	S_Δ[c]	a[c]
tetraphenylporphine zinc	0.88[a]	0.871	0.55	
octaethylporphine zinc	1.00[b]	1.98	0.40	0.39
1-pyrenecarboxaldehyde	0.78[a]	1.71	0.90	0.70
chrysene	0.85[a]	1.35	0.60	0.31
C_{60}	1.00[a]	1.43	0.74	
C_{70}	0.97[a]	0.793	0.65	
benzo[*h*]quinoline	0.88[a]	1.40	0.60	0.48
quinoxaline	0.99[a]	0.65	0.95	0.88
tetrachloro-*p*-benzoquinone	0.98[a]	1.32	0.91	0.74

[a] Reference 64. [b] Determined by photoacoustic calorimetry, ±3%. [c] ±10%.

Results and Discussion

All newly determined oxidation potentials are listed in Table 1, together with the corrsponding gas-phase ionization energies IE.

No peaks were observed with three compounds used in this study, namely, quinoxaline, duroquinone, and tetrachloro-*p*-benzoquinone. A correlation between E_{ox} values and gas-phase ionization energies IE is used to estimate their oxidation potentials (see Figure 2, estimated values are listed in Table 1). All IE data have been taken from http://webbook.nist.gov. We use "evaluated IE" values, when such values are given, and mean values of all listed IE determinations in all other cases. We will consider below experimental data for a series of naphthalene and biphenyl derivatives, for which all E_{ox} data have been measured by Abdel-Shafi and Wilkinson,[11,16] using a SCE reference electrode, in deoxygenated acetonitrile solutions containing 10^{-3} M of the respective derivative, and 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. We have previously noted a systematic shift of 0.09 V between these data and our values measured with tetrabutylammonium-hexafluorophosphate vs Ag/AgCl reference electrode.[21] All new data are converted accordingly, and SCE values are used for calculations of ΔG_{CET}, according to eq 10, where C is neglected.

Newly determined photophysical data for a series of sensitizers with strongly varying E_{ox}, E_T and molecular structure are listed in Table 2. These data can be used to calculate the rate constants of formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$, according to eqs 1−4. All calculated k_T^P values are listed in Table 3, together with the respective data for all previously

TABLE 3: Rate Constants $k_T{}^1\Sigma_g$, $k_T{}^1\Delta_g$, and $k_T{}^3\Sigma_g^-$ of Formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ during O_2 Quenching of Triplet Excited Sensitizers and the Corresponding Triplet Energies E_T and Free Energies ΔG_{CET} for a Complete Electron Transfer

sensitizer	E_T kJ mol^{-1}	ΔG_{CET} kJ mol^{-1}	$k_T{}^{1\Sigma}$ 10^9 s^{-1}	$k_T{}^{1\Delta}$ 10^9 s^{-1}	$k_T{}^{3\Sigma}$ 10^9 s^{-1}
tetraphenylporphine zinc	153[a]	15		0.49	0.40
octaethylporphine zinc	170[a]	−3	0.83		1.28
1-pyrenecarboxaldehyde	180[a]	35	1.28	0.36	0.18
chrysene	239[a]	−13	0.44	0.41	0.57
C_{60}	148[b]	88		1.12	0.39
C_{70}	131[b]	105		0.53	0.29
benzo[*h*]quinoline	260[a]	−10	0.71	0.18	0.59
quinoxaline	255[a]	50	0.59	0.05	0.03
tetrachloro-*p*-benzoquinone	206[a]	144	1.03	0.24	0.12
tetraphenylporphine[c]	140	35[d]		1.12	0.41
9-bromanthracene[c]	168	43[d]	1.32	1.51	0.31
phenalenone[c]	186	78[d]	1.44	0.89	0.07
phenazine[c]	186	83[d]	1.38	0.44	0.08
acridine[c]	189	46[d]	1.44	0.66	
benzanthrone[c]	205	30[d]	1.60	0.28	
9-fluorenone[c]	223	56[d]	1.75	0.14	0.06
duroquinone[c]	235	82[d]	1.18	0.37	0.12
2-acetonaphthone[c]	248	21[d]	1.01	0.21	0.18
4-benzoylbiphenyl[c]	254	27[d]	0.53	0.05	0.10
triphenylene[c]	278	−38[d]	0.30		0.73
1-methoxynaphthalene[e]	256	−59	1.80	0.49	2.10
acenaphthene[e]	250	−46	1.51	0.36	1.30
2-methoxynaphthalene[e]	253	−45	1.63	0.29	0.64
2,6-dimethylnaphthalene[e]	252	−33	1.59	0.16	0.45
1-methylnaphthalene[e]	257	−33	1.28	0.19	0.35
2-methylnaphthalene[e]	253	−22	1.31	0.18	0.27
naphthalene[e]	255	−21	1.12	0.11	0.17
1-bromonaphthalene[e]	247	−1	1.10	0.11	0.02
1-cyanonaphthalene[e]	243	26	0.81	0.12	0.02
4,4′-dimethoxybiphenyl[f]	266	−65	4.45	1.86	13.31
4-methoxybiphenyl[f]	270	−47	1.47	0.33	3.14
4,4′-dimethylbiphenyl[f]	269	−31	1.31	0.26	0.95
4-methylbiphenyl[f]	272	−23	0.91	0.18	0.46
biphenyl[f]	274	−15	0.61	0.10	0.31
4-chlorobiphenyl[f]	269	−5	0.65	0.10	0.15
4-bromobiphenyl[f]	266	−3	0.64	0.08	0.12
4,4′-dibromobiphenyl[f]	265	4	0.70	0.05	0.06
4,4′-dichlorobiphenyl	265	5	0.62	0.09	0.10
4-cyanobiphenyl[f]	265	14	0.54	0.07	0.05
2-methylfluorene[g]	282	−59	0.68	0.24	1.42
1-methylfluorene[g]	284	−54	0.60	0.31	2.28
fluorene[g]	285	−51	0.86	0.42	2.53
2-bromofluorene[g]	276	−36	0.61	0.16	1.04
2,7-dibromofluorene[g]	270	−18	0.47	0.13	0.52
2,4,7-trichlorofluorene[g]	273	−9	0.38	0.06	0.22

[a] Reference 64. [b] Reference 65. [c] Reference 34. [d] This work. [e] Reference 16. [f] Reference 17. [g] Reference 18.

investigated sensitizers[16−18] and the corresponding ΔG_{CET} and E_T data.

Figure 3 shows the dependence of all multiplicity-normalized $k_T{}^{1\Sigma}$, $k_T{}^{1\Delta}$, and $k_T{}^{3\Sigma}$ values on ΔE and ΔG_{CET} and thus on E_T and E_{ox}. It is shown that the whole data set, which covers the ΔE and ΔG_{CET} range of most natural and synthetic sensitizers, and includes aromatic hydrocarbons composed of very variable numbers of five- and/or six-membered rings, with and without heteroatoms, or even metal centers, and bearing many different types of substituents, is described by one surface calculated using eqs 6−8, where the nCT and CT contributions have been estimated by eqs 9 and 11, with $c_1 = 7.65$ and $c_2 = 0.023$ mol kJ^{-1}. (For clarity reasons, eq 11 was approximated using $c^P/m = 1$ for formation of all three O_2 product states. The actual model predicts three distinct but closely lying surfaces, for formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$, respectively, and describes the data better than represented in Figure 3. Standard deviation of experimental vs calculated data of $\log(k_T{}^P/m)$ amounts to 0.27, which corresponds to a factor of 1.8 in $k_T{}^P/m$, which is rather small, if the overall variation of $k_T{}^P/m$ by the factor of 750 is considered.)

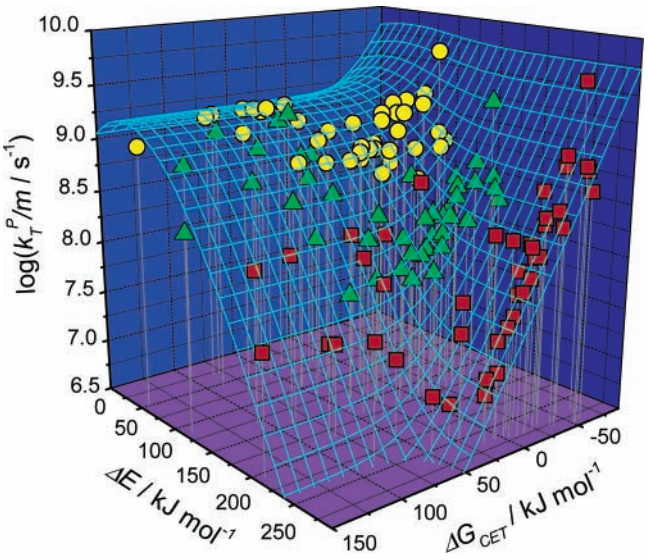

Figure 3. Dependence of the multiplicity-normalized rate constants $k_T{}^P/m$ of formation of $O_2(^1\Sigma_g^+)$ (circles), $O_2(^1\Delta_g)$ (triangles), and $O_2(^3\Sigma_g^-)$ (squares) during O_2 quenching of $\pi\pi^*$ triplet states on the excess energy ΔE for formation of the respective O_2 product state and the free energy ΔG_{CET} for formation of an ion pair. Surface calculated by $k_T{}^P/m = k_{\Delta E}{}^P/m + k_{CT}{}^P/m$, using $\log(k_{\Delta E}{}^P/m) = 9.05 + 9 \times 10^{-3}\,\Delta E - 1.15 \times 10^{-4}\,\Delta E^2 + 1.15 \times 10^{-7}\,\Delta E^3 + 9.1 \times 10^{-11}\Delta E$,[4] and $\log(k_{CT}{}^P/m) = 7.65 - 0.023\Delta G_{CET}$.

However, deviations of experimental from calculated data are in part larger than the experimental uncertainties. This is most probably a result of the general neglect of the electrostatic interaction energy C, which is positive in the nonpolar solvent CCl_4 and which depends on the widely varying molecular structure of the sensitizers. An additional but less important source of uncertainty of the values of ΔG_{CET} results from the uncertainty of the E_{ox} data. Nonetheless, the description of the data by eqs 6−11 is still surprisingly good, and we demonstrate clearly that E_T and E_{ox} are by far the most important parameters determining $k_T{}^{1\Sigma}$, $k_T{}^{1\Delta}$, and $k_T{}^{3\Sigma}$. This also means that the mechanism of singlet oxygen photosensitization via nCT and CT complexes described in Figure 1 can be generally applied to $\pi\pi^*$ excited triplets. Figure 3 shows that the nCT path dominates for sensitizers with $\Delta G_{CET} \geq 50$ kJ mol^{-1}, i.e., on the left-hand side. The additional quenching via the pCT channel becomes only important in the exergonic range and dominates for sensitizers with $\Delta G_{CET} \leq -25$ kJ mol^{-1}, i.e., on the right border of the calculated surface.

The general validity of the model also shows that eqs 6−11 can be used to estimate the rate constants and efficiencies of singlet oxygen formation during O_2 quenching of T_1 states of $\pi\pi^*$ excited aromatic hydrocarbons as a function of sensitizer E_{ox} and E_T. The rate constants of formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ can be simply calculated from eqs 6−11, and since deactivation of $O_2(^1\Sigma_g^+)$ to $O_2(^1\Delta_g)$ is a quantitative process, the overall efficiency S_Δ of singlet oxygen formation, which is the relevant parameter in most applications, can be calculated by eq 12

$$S_\Delta = \frac{k_T{}^{1\Sigma} + k_T{}^{1\Delta}}{k_T{}^{1\Sigma} + k_T{}^{1\Delta} + k_T{}^{3\Sigma}} \qquad (12)$$

Because of the extremely short lifetime of $O_2(^1\Sigma_g^+)$ in most

solvents,[2] the measurements described in this work have so far only been possible in solutions of CCl_4, and thus, the direct application of our results is only valid in this solvent. However, it is well-established that medium-dependent variations of k_T^Q and S_Δ exhibit a systematic dependence on solvent polarity. It has been reported that k_T^Q for several series of sensitizers increases significantly with increasing solvent polarity, while S_Δ decreases.[8,9,12,15,19−21,31] Hence, the present model can be used to estimate relative values in other media. Although other parameters, such as sensitizer aggregation (which was generally found to diminish the singlet oxygen yield of a sensitizer)[50−53] might come into play in several media, and especially in biological situations, it is believed that the relations presented here will be most useful for the optimization of the inherent properties of molecules with regard to their singlet oxygen photosensitization ability and, thus, also for the development of efficient singlet oxygen sensitizers for several applications. One important restriction, however, needs to be made: The correlation does not apply to $n\pi^*$ excited triplets, where a different quenching mechanism operates.[21,49]

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