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Effect of Charge-Transfer Interactions on the Radiative Rate Constant of $^1\Delta_g$ Singlet Oxygen

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The radiative rate constant (k_r) and the lifetime of singlet oxygen were measured in 17 new solvents with low and high ionization potentials (IP) using an IR laser fluorimeter. Analysis of the values of $k_r = 0.1-3.1$ s^{-1} in 63 solvents shows that the charge-transfer interaction is the main factor in removal of the prohibition on the radiative spin-forbidden transition $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ in oxygen and leads to an increase in the k_r values in solvents with low ionization potentials. There is no correlation of k_r with the energy of dispersion interactions in collision complex $O_2(^1\Delta_g)\cdots$solvent. The averaged contribution of the dispersion interactions in the k_r dependence on the nature of solvent is estimated at 10%.

Introduction

The transition $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ in molecular oxygen, which is strongly spin-, symmetry-, and parity-forbidden, results in a very low value of the luminescence rate constant in a vacuum $k_r = 2.6 \times 10^{-4}$ s^{-1}.[1] In solution, this prohibition is partially removed and results in a sharp increase of the radiative rate constant $k_r \approx 0.1-1$ s^{-1}.[2]

In 1973, Long and Kearns[2] explained the enchancement of the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition in oxygen by taking into account the exchange mixing of the $^1\Delta_g$ state with the higher excited states of a [$O_2\cdots$solvent] collision complex. It was pointed out by Hurst, McDonald, and Schuster in 1982 that the k_r value should depend strongly on the nature of the solvent.[3] Quantitative estimates of k_r were obtained later by several authors.[4−10]

There are currently two views on the nature of the interactions responsible for the removal of the prohibition on the radiative $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition in oxygen and solvent effect.[5,9,11−13] For a limited series of solvents, empirical quadratic correlations of k_r vs P and k_r/S vs P/S were established,[5,11,12] where n is the refractive index, $P = (n^2 - 1)/(n^2 + 2)$, the solvent polarizability, and S is the solvent molarity. The authors concluded that dispersion interactions are the main factor leading to the k_r dependence on the solvent nature.[5,9,11,12] Dispersion interactions are a universal type of interaction and are always present between any two reagents in an encounter complex.

In contrast to this conclusion is the notion that charge-transfer interactions are the dominant factor in removal of the prohibition on the spin-forbidden radiative $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition in oxygen.[13] Theoretical calculations show that the charge-transfer interactions efficiently mix the $^1\Delta_g$ and $^3\Sigma_g^-$ states, increasing the spin−orbit coupling in the [$O_2^{-\delta}\cdots$solvent$^{+\delta}$] complex, and should lead to an increase of the k_r value in solvents with the low ionization potentials.[14,15] We previously proposed that this is the dominant solvent affecting regarding k_r,[13] based on a linear dependence of $\log(k_r/n^2)$ vs IP for solvents with IPs below 11 eV, where IP is the ionization potential of a solvent molecule in a gas phase. For organic solvents, $P \approx n^2$. Thus, use of the ratio k_r/n^2 allows for the accounting of the contribution of the dispersion interactions from the k_r dependence on the solvent nature.

To clarify this question, we measured the radiative rate constant of $O_2(^1\Delta_g)$ in 17 new solvents with low and high ionization potentials. The dependence of k_r on the dispersion and charge-transfer interactions with the solvent is discussed.

Experimental Section

The yield (A_o) and decay kinetics of $O_2(^1\Delta_g)$ luminescence at 1.27 μm were recorded 90° to the laser beam with a time-resolved fluorimeter described elsewhere.[16] We used a TDS-250 digitizing oscilloscope interfaced to a Macintosh with Igor software for data collection. Air-saturated solutions of sensitizers were excited in a 1 cm quartz cell with laser pulses $\lambda_{ex} = 532$ (or 355) nm, 5 ns, 5 mJ, from a Continuum Surelite Nd:YAG laser. The optical densities of solutions at the excitation wavelength were $OD_{532} \approx 0.2$.

The determination of k_r values was carried out using eq 1 by comparing the $O_2(^1\Delta_g)$ luminescence intensity extrapolated to the center of the laser pulse (A_o) for the same sensitizer in the investigated solvent and in benzene as a standard solvent[4]

$$k_r = \frac{\Phi_\Delta^{\ st} A_o (1 - 10^{-OD_{532}^{\ st}})\, n^2}{\Phi_\Delta A_o^{\ st} (1 - 10^{-OD_{532}})\, n^2_{\ st}} k_r^{\ st} \tag{1}$$

where k_r is the $O_2(^1\Delta_g)$ radiative rate constant in the investigated solvent, $k_r^{st} = k_r(C_6H_6) = 1.5$ s^{-1},[12] and Φ_Δ is the quantum yield of $O_2(^1\Delta_g)$ generation by the sensitizer. We observed that in air-saturated solvents except for CH_2I_2, the triplet sensitizer lifetime decreases by at least 20 times; therefore, any correction of eq 1 for incomplete triplet-state quenching by O_2 is insignificant. In CH_2I_2, this correction was carried out.

The sensitizers used were 5,10,15,20-tetraphenylporphine (TPP), buckminsterfullerene (C_{60}), and perinaphthenone (PN). All were purchased from Aldrich and used as received. Solvents were the best grade available from Fisher Scientific or Aldrich and were purified by distillation. All experiments were carried out at 23° C. Absorption spectra were recorded with a UV-2101 PC Shimadzu spectrophotometer.

Results

We have assumed that the quantum yield of $O_2(^1\Delta_g)$ generation by each sensitizer is constant in all of the solvents studied.

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TABLE 1: Lifetime and Radiative Rate Constant of $O_2(^1\Delta_g)$ in Different Solvents

solvent	I_{ion},[a] eV	τ_Δ, μs	k_r,[b] s^{-1}			$\langle k_r \rangle$,[c] s^{-1}
			TPP	C_{60}	PN	
1-methylnaphthalene	7.85	7.1	2.18	2.63		2.4
1,3-dimethoxybenzene	8.0[d]	1.9	1.91	1.82		1.9
phenyl ether	8.09	17	1.92		2.04[e]	2.0
1,2,4-trimethylbenzene	8.27[i]	9.5	2.1	1.9		2.0
anisole	8.21	9.8	1.81	1.79		1.8
mesitylene	8.41	15	1.8	1.64		1.72
p-xylene	8.44	19	1.61	1.81		1.7
p-bromoanisole	8.49	16	1.84	1.95		1.9
p-chloroanisole	8.5[f]	15	2.07	2.37		2.2
toluene-d_8	8.82[i]	290	1.45	1.49		1.47
CH_2I_2	9.46	15	2.0			2.0
acetic anhydride	10.0	53	0.5		0.56[e]	0.53
CS_2	10.07	3000	2.1	2.17		2.14
hexane	10.13	28	0.51		0.68[e]	0.6
pentane	10.35	35	0.54[e]		0.40[e]	0.47
CH_2Br_2	10.50	60		0.85	0.75	0.8
propionic acid	10.525	25		0.83[e]	0.75	0.79
2-nitropropane	10.71	33	0.175[g]	0.20[h]		0.19
1,2-dichloroethane	11.04	63		0.66	0.84[e]	0.75
formic acid	11.33	25	0.3[g]		0.2[e]	0.25
CCl_4	11.47	1000		1.0[e]	0.82[e]	0.91

[a] Reference 21. [b] Experimental k_r value for different sensitizers. [c] Average value. [d] Estimated according to the oxidation potential $E_{1/2}^{ox} = 1.49$ V vs SCE[22] compared with data for naphthalene ($E_{1/2}^{ox} = 1.54$ V vs SCE;[23] I_{ion}=8.14 eV) and 1-methylnaphthalene ($E_{1/2}^{ox} = 1.43$ V vs SCE;[23] $I_{ion} = 7.85$ eV). [e] $\lambda_{ex} = 355$ nm. [f] Estimated according to the oxidation potential $E_{1/2}^{ox} = 1.72$ V vs SCE[24] compared with data for *p*-bromoanisole ($E_{1/2}^{ox} = 1.70$ V vs SCE;[24] $I_{ion} = 8.49$ eV). [g] Sensitizer is protoporphyrin IX dimethyl ester. [h] OD_{532}=0.06. [i] Assumed equal to protonated solvent.

This approach is supported by experimental data in the literature where for TPP, $\Phi_\Delta = 0.64 \pm 0.13$ in the 19 solvents studied.[9] It was established that for C_{60}, $\Phi_\Delta \approx 1.0$ in benzene, toluene and cyclohexane.[17−19] This estimate was successfully used previously to measure the k_r values in several solvents.[11] It has been shown that PN generates singlet oxygen with $\Phi_\Delta = 0.94{-}1.0$ in 13 various solvents and methanol−H_2O mixtures.[20]

Thus, using the approach $\Phi_\Delta = \Phi_\Delta^{st}$(benzene) and eq 1, we determined k_r values in 14 new solvents (Table 1). The values k_r in CCl_4 and CS_2 were the subject of some controversy, and we remeasured these values in this work. Our estimate $k_r = 2.14$ s^{-1} in CS_2 (Table 1) is in good agreement with the experimental result of 2.7 s^{-1} recently obtained by Scurlock.[11] The value of $k_r = 0.91$ s^{-1} in CCl_4 (Table 1) is in excellent agreement with the previously reported value of 0.93 s^{-1}.[9]

We have also measured the $O_2(^1\Delta_g)$ lifetimes in the solvents shown in Table 1. The τ_Δ values in mesitylene, *p*-xylene, pentane, and 1,2-dichloroethane were known in the literature[28] and are in good agreement with the present results.

Discussion

The radiative rate constant of $O_2(^1\Delta_g)$ may be estimated from the well-known expression of Strickler and Berg[29]

$$k_r = (2.88 \times 10^9) n^2 \nu_o{}^2 \frac{g_l}{g_u} \int \epsilon \, d\nu \tag{2}$$

where $\nu_o = 7850$ cm^{-1} and is the averaged frequency of the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition,[30] g_l and g_u are the degeneracies of the $^3\Sigma_g^-$ and $^1\Delta_g$ states, and ϵ is the extinction coefficient of molecular oxygen. The integral extends over the entire $^3\Sigma_g^- \rightarrow {}^1\Delta_g$ absorption band. Unfortunately, eq 2 cannot be used to directly estimate k_r because ϵ values for oxygen have not been reported.

Let us consider, therefore, a practical analysis. The increase of the solvent polarizability leading to an increase of the induced dipole moment of the $^3\Sigma_g^- \rightarrow {}^1\Delta_g$ transition should lead to an increase of the k_r value, in total agreement with eq 2. Equation 2 predicts a linear dependence of k_r on P. However, the function P is only a qualitative estimate which does not take into account such parameters as the size of molecules, molecular polirzability of solvent molecules, and internuclear distance in collision complex.[31] More properly, a dependence of k_r on the *energy* of the disperion interaction (ΔV) is expected. The ΔV value, which takes into account all of the above-mentioned variables, is a universal quantitative parameter directly proportional to the radiative rate constant, i.e., $k_r \approx p^2 \approx |\Delta V|$, where p is an induced dipole moment of the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition.[31]

For an estimate of the effect of dispersion interactions, we will analyze the dependence of k_r on the energy of dispersion interactions between $O_2(^1\Delta_g)$ and solvent molecule using the London formula[21,32]

$$\Delta V = -1.5 \alpha_s' \alpha_\Delta' d_c^{-6} (\mathrm{IP}) I_\Delta / (\mathrm{IP} + I_\Delta) \tag{3}$$

where I_Δ is the ionization potential of oxygen in the $^1\Delta_g$ state: $I_\Delta = \mathrm{IP}(O_2) - \mathrm{E}(^1\Delta_g) = 12.07 - 0.98 = 11.09$ eV.[21,33]

The molecular polarizability α_s' of a solvent molecule is given by the Lorenz−Lorentz equation[21,31]

$$\alpha_s' = \frac{3P}{4\pi SN} \tag{4}$$

where S the the solvent molarity and N is Avogadro's number. The experimental molecular polarizability of oxygen in the ground state is 1.58 Å^3.[21] For singlet oxygen, this value is unknown and we will use the estimate $\alpha_\Delta' = 2.6$ Å^3 of Schmidt.[34] We assume a spherical form of molecules in order to estimate the internuclear distance d_c in the collision complexes and use the known radius of singlet oxygen of 1.216 Å.[33] The estimates of ΔV for all solvents studied in the literature are given in Table 2. It is necessary to note that the theoretical estimates of α_S' values from eq 4 are in a good agreement with the known experimental data.[21] The dispersion interaction is very weak, and $|\Delta V|$ values are near kT.

From the data shown in Figure 1, it follows that there is no correlation between the radiative rate constant and the energy

TABLE 2: Photophysical Properties of $O_2(^1\Delta_g)$ in Different Solvents

solvent	n	I_{ion},[a] eV	S, M	d_c, Å	α_s', Å^3	$-\Delta V$, cm^{-1}	k_r,[b] s^{-1}
Ph_2S	1.6327	7.81	6.00	5.26	23.61	160	2.66
1-methylnaphthalene	1.615	7.85	7.04	5.05	19.66	171	2.68[c]
2-ethylnaphthalene	1.598	7.9[d]	6.35	5.18	21.31	159	2.025
1,3-dimethoxybenzene	1.524	8.0	7.64	4.95	15.89	159	1.9[e]
phenyl ether	1.579	8.09	6.30	5.19	20.91	157	2.0[e]
1-bromonaphthalene	1.657	8.09	7.19	5.02	20.29	186	3.11
1,2,4-trimethylbenzene	1.504	8.27	7.40	4.99	15.88	153	2.0[e]
anisole	1.516	8.21	9.20	4.72	13.02	174	1.8[e]
mesitylene	1.449	8.41	7.19	5.02	16.20	152	1.72[e]
p-xylene	1.495	8.44	8.16	4.87	14.18	161	1.7[e]
p-bromoanisole	1.564	8.49	7.99	4.89	16.15	178	1.9[e]
p-chloroanisole	1.535	8.5	8.16	4.87	15.13	173	2.2[e]
C_6H_5I	1.620	8.69	8.94	4.76	15.59	206	2.61
toluene	1.496	8.82	9.39	4.70	12.43	177	1.44
toluene-d_8	1.4932	8.82	9.41	4.70	12.25	177	1.47[e]
C_6H_5Br	1.559	8.98	9.50	4.69	13.49	199	1.97
1,3-dibromobenzene	1.608	9.05	8.27	4.85	16.58	200	2.715
C_6H_5Cl	1.524	9.06	9.84	4.65	12.34	193	1.68
N,*N*-dimethylformamide	1.4305	9.13	12.91	4.35	7.94	185	0.63[f]
dioxane	1.4225	9.19	11.73	4.45	8.61	175	0.56
C_6H_5F	1.465	9.20	10.66	4.56	10.29	182	1.28
benzene	1.501	9.25	11.19	4.50	10.44	199	1.5[g]
benzene-d_6	1.4986	9.25[l]	11.29	4.49	10.30	199	1.34[g]
1-iodopropane	1.504	9.27	10.25	4.60	11.46	193	1.44[g]
tetrahydrofuran	1.407	9.41	12.33	4.40	7.92	176	0.77[g]
CH_2I_2	1.743	9.46	12.41	4.39	12.93	290	2.0[e]
C_6F_5I	1.497	9.50	7.50	4.97	15.48	165	1.23[g]
diethyl ether	1.353	9.51	9.55	4.68	9.00	138	0.615[f]
C_6F_5Br	1.449	9.57	8.02	4.89	13.26	157	1.25[g]
benzonitrile	1.528	9.62	9.79	4.65	12.47	200	1.8
$CF_3C_6H_5$	1.414	9.685	8.21	4.86	12.08	149	1.14
acetone	1.598	9.71	13.62	4.29	6.41	167	0.59
C_6F_5Cl	1.421	9.72	7.74	4.93	12.99	148	0.89[g]
cyclohexane	1.426	9.86	9.26	4.72	10.98	164	0.66
2-butanol	1.3975	9.88	10.90	4.53	8.77	167	0.57[f]
C_6F_6	1.3769	9.906	8.66	4.79	10.53	143	0.51[g]
heptane	1.387	9.92	6.83	5.09	13.68	130	0.66
acetic anhydride	1.390	10.0	10.60	4.56	8.87	163	0.53[e]
1-butanol	1.3985	10.06	10.93	4.53	8.77	169	0.465[f]
CS_2	1.627	10.07	16.59	4.10	8.47	298	2.14[e]
2-propanol	1.377	10.12	13.06	4.34	6.99	175	0.465
hexane	1.375	10.13	7.65	4.94	11.87	135	0.6[e]
formamide	1.447	10.16	25.18	3.72	4.21	268	0.36[f]
1-propanol	1.384	10.22	13.38	4.31	6.93	181	0.53[f]
pentane	1.358	10.35	8.68	4.79	10.04	140	0.47[e]
CH_3CH_2OD	1.3595	10.47	17.01	4.07	5.14	191	0.35
ethanol	1.360	10.47	17.04	4.07	5.14	191	0.55[f]
CH_2Br_2	1.541	10.50	14.25	4.24	8.75	253	0.80[e]
propionic acid	1.386	10.525	13.40	4.31	6.95	184	0.79[e]
2-nitropropane	1.394	10.71	11.13	4.51	8.52	174	0.19[e]
methanol	1.329	10.85	24.69	3.74	3.27	206	0.32
methanol-d_4	1.3262	10.98[h]	24.62	3.74	3.25	206	0.30[i]
1,2-dichloroethane	1.445	11.04	12.69	4.37	8.32	209	0.75[e]
$C_2F_4Br_2$	1.370	11.1	8.37	4.84	10.72	164	1.4[g]
CH_2Cl_2	1.424	11.32	15.60	4.16	6.49	221	0.75
formic acid	1.3704	11.33	26.50	3.68	3.39	240	0.25[e]
$CHCl_3$	1.446	11.37	12.50	4.38	8.46	211	1.14
CCl_4	1.4595	11.47	10.36	4.59	10.47	200	0.92[j]
CF_3CH_2OH	1.290	11.7	13.73	4.29	5.24	152	0.17
$C_2Cl_3F_3$	1.3578	11.99	6.18	5.22	14.10	126	1.35[g]
acetonitrile	1.344	12.194	19.15	3.96	4.39	207	0.45
D_2O	1.328	12.6	55.27	3.15	1.46	279	0.18
H_2O	1.333	12.612	55.41	3.14	1.47	283	0.10[k]

[a] Reference 21. [b] Averaged values from the literature data in ref 11 taking into account $k_r(C_6H_6) = 1.5$ s^{-1} [9]. [c] Averaged value from 2.96 s^{-1} [9] and 2.4 s^{-1} of this work. [d] Reference 11. [e] This work. [f] Reference 4. [g] Reference 9. [h] Reference 25. [i] References 8 and 10. [j] Averaged value of 0.93 s^{-1} [9] and 0.91 s^{-1} in this work. [k] The averaged value of published data are 0.18,[9] 0.075,[8,10] 0.06,[13] and 0.066 s^{-1}.[26] [l] Reference 27.

of dispersion interactions. We interpret this to mean that other interactions are responsable for the strong k_r dependence on the solvent nature.

This lack of correlation led us to estimate the contribution of charge-transfer interactions to the k_r dependence on the solvent nature. Singlet oxygen is a good electron acceptor (the electron affinity of O_2 is 0.45 eV[21]), so the solvent molecules should act as electron donors. To subtract the dependence of the k_r value on the energy of dispersion interactions, we will analyze the data from a plot of $\log(k_r/|\Delta V|)$ vs IP. From the

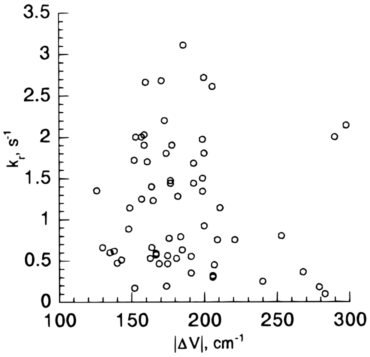

Figure 1. Dependence of the $O_2(^1\Delta_g)$ radiative rate constant on the energy of dispersion interactions.

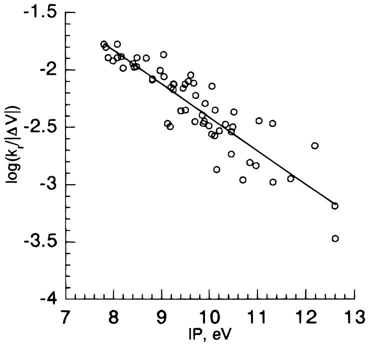

Figure 2. Dependence of $\log(k_r/|\Delta V|)$ on the ionization potential of the solvent. Linear least-squares fit: slope is -0.292 eV^{-1}, intercept is 0.512, and correlation coefficient is 0.897.

data presented in Figure 2, we conclude that despite the different solvent nature and accuracy of k_r measurements, there is a good linear dependence of $\log(k_r/|\Delta V|)$ vs IP. A slope of -0.3 eV^{-1} with the correlation coefficient 0.90 is obtained.

The only solvents not included in the plot are CCl_4, $CHCl_3$, $C_2H_4Br_2$, and $C_2Cl_3F_3$, which are all in the region IP $>$ 11 eV. Carbon tetrachloride and chloroform are very powerful electron acceptors, and we estimated that in a collision complex with $O_2(^1\Delta_g)$, these species act as electron acceptors.[13] This means that, as a matter of principle, we cannot use the data in these solvents to fit the dependence $\log(k_r/|\Delta V|)$ vs IP. The electron affinities of $C_2H_4Br_2$ and $C_2Cl_3F_3$ are unknown; however, it is reasonable to expect them to be high. Nonetheless, at present, the physical reasons for high k_r values in four above-mentioned solvents is not clear, and additional investigations are required in the region IP $>$ 11 eV.

The small slope of the linear dependence in Figure 2, -0.3 eV^{-1}, points out that in an encounter complex, the weak exciplex with a partial electron transfer $[O_2(^1\Delta_g)^{-\delta}\cdots\text{solvent}^{+\delta}]$ is formed. Thus, we conclude that charge-transfer interactions are responsible for removal the prohibition on the radiative spin-forbidden $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition in oxygen and lead to the high values of k_r in solvents with low ionization potentials. According to the data in Figure 2 and the value of k_r in a vacuum,[1] the next semiempirical equation may be offered

$$k_r = 2.6 \times 10^{-4} + 3.27|\Delta V|e^{-0.67\mathrm{IP}} \tag{5}$$

or in the simplified Strickler–Berg form, which is convinient for practical estimates,

$$k_r = 2.6 \times 10^{-4} + 63.3n^2 e^{-0.52\mathrm{IP}} \tag{6}$$

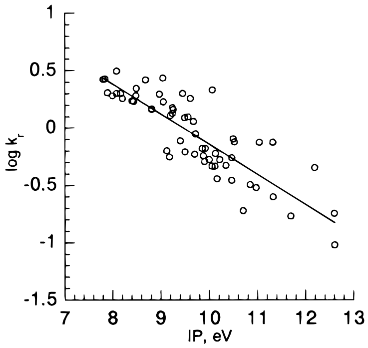

Figure 3. Dependence of the $O_2(^1\Delta_g)$ radiative rate constant on the ionization potential of the solvent. Linear least-squares fit: slope is -0.262 eV^{-1}, intercept is 2.483, and correlation coefficient is 0.855.

where k_r is in s^{-1}, ΔV is in cm^{-1}, and IP is in eV.

We can roughly estimate the contribution of the dispersion interactions by analysis of the experimental data plotted in coordinates of log k_r vs IP (Figure 3). In this case, we obtain the linear dependence with a smaller slope is -0.26 eV^{-1} and a lower correlation coefficient than those of Figure 2. Comparing the slopes of linear dependences in Figures 1 and 2, we estimate the contribution of dispersion interactions as ~10%. Thus, the effect of the dispersion interaction inducing the dipole moment in the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition is small in comparison with the charge-transfer interactions.

Plots of k_r vs P were interpreted in the literature as showing a strong dependence on the polarizability.[5,9,11,12] However, as previous authors have also pointed out, there is a qualitative inverse correlation between the ionization potential of a solvent and P (Table 2). Thus, we note, as others have, that k_r is bound to have a qualitative correlation with both IP and P. It is our interpretation, however, that the IP correlation makes more physical sense, particularly in light of the results shown in Figure 1. Furthermore, the correlations of k_r with n or P are not nearly as strong as those previously reported with a larger sample of solvents.

It is interesting to note that heavy-atom effects on the k_r value are not observed (Table 2). For halogen-substituted benzenes and anisoles, the value of k_r is determined mainly by the IP value rather than the presence of a heavy atom in the solvent molecule. In organic solvents, $k_r = 0.1-3.1$ s^{-1}, much higher than in a vacuum 2.6×10^{-4} s^{-1}.[1] This suggests that the $^1\Delta_g$ and $^3\Sigma_g^-$ states are significantly mixed through the charge-transfer interactions with the solvent, and therefore, the contribution of heavy-atom effect must be a much smaller perturbation.

Minaev[15,35,36] predicted that probability of the $a^1\Delta_g \rightarrow X^3\Sigma_g^-$ radiative transition in molecular oxygen should increase in collisions with solvents molecules. It is proposed that the a → X transition borrows intensity from the collision-induced $b^1\Sigma_g^+ \rightarrow a^1\Delta_g$ transition due to the spin–orbit interaction in oxygen. The ratio of the collision-induced b → a and a → X radiative rate constants for molecular oxygen in CCl_4 was determined by Schmidt and Bodesheim[37] and equals is 3.2×10^{-4}, in good agreement with the theoretical estimate.[36] According to this model, one can expect that in solvents with heavy atoms, the strong spin–orbit coupling in collision complex $O_2\cdots$solvent should lead to the increase of the a → X radiative rate constant. However, as mentioned above, this effect is not observed experimentally (Table 2). We can suppose that the mechanism of the a → X transition enhancement through the intensity borrowing from the b → a transition may be the main factor in rare gas matrixes and in solvents with high ionization potentials, where the contribution of the charge-transfer interaction is negligible.

Summary

The charge-transfer interaction between $O_2(^1\Delta_g)$ and solvent molecules is the major factor in the removal of the prohibition on the spin-forbidden radiative transition $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ in oxygen. The mixing of the charge-transfer state with the $^1\Delta_g$ and $^3\Sigma_g^-$ states of oxygen leads to a strong increase of spin−orbit coupling in the exciplex $[O_2^{-\delta}\cdots\text{solvent}^{+\delta}]$, which results in an increase of the radiative rate constant in solvents with a low ionization potential. The contribution of dispersion interactions is estimated to be small (∼10%) in comparison with the effect of the charge-transfer interactions.

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References and Notes

(1) Badger, R.; Wright, A.; Whitlock, R. *J. Chem. Phys.* **1965**, *43*, 4345.

(2) Long, C.; Kearns, D. R. *J. Chem. Phys.* **1973**, *59*, 5729.

(3) Hurst, J. R.; McDonald, J. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 2065.

(4) Darmanyan, A. P. *Khim. Fiz.* **1987**, *6*, 1192.

(5) Scurlock, R. D.; Ogilby, P. R. *J. Phys. Chem.* **1987**, *91*, 4599.

(6) Gorman, A. A.; Hamblett, I.; Lambert, C.; Prescott, A. L.; Rodgers, M. A. J.; Spence, H. *J. Am. Chem. Soc.* **1987**, *109*, 3091.

(7) Krasnovskii, A. A.; Yegorov, S. Y.; Nazarova, O. V.; Yartsev, Y. I.; Ponomarev, G. V. *Biofizika* **1987**, *32*, 982.

(8) Losev, A. P.; Byteva, I. M.; Gurinovich, G. P. *Chem. Phys. Lett.* **1988**, *143*, 127.

(9) Schmidt, R.; Agshari, E. *J. Phys. Chem.* **1990**, *94*, 4377.

(10) Losev, A. P.; Nichiporevich, I. N.; Byteva, I. M.; Drozdov, N. N.; Al Jghgami, I. F. *Chem. Phys. Lett.* **1991**, *181*, 45.

(11) Scurlock, R. D.; Nonell, S.; Braslavsky, S. E.; Ogilby, P. R. *J. Phys. Chem.* **1995**, *99*, 3521.

(12) Schmidt, R.; Bogesheim, M. *J. Phys. Chem.* **1995**, *99*, 15919.

(13) Darmanyan, A. P. *Chem. Phys. Lett.* **1993**, *215*, 477.

(14) Minaev, B. F. *Theor. Exp. Chem.* **1984**, *20*, 199.

(15) Minaev, B. F. *Opt. Spectrosc.* **1985**, *58*, 761.

(16) Darmanyan, A. P.; Tatikolov, A. S. *J. Photochem.* **1986**, *32*, 157.

(17) Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 11.

(18) Hung, R. R.; Grabowski, J. J. *J. Phys. Chem.* **1991**, *95*, 6073.

(19) Terazima, M.; Hirota, N.; Shinohara, H.; Saito, Y. *J. Phys. Chem.* **1991**, *95*, 9080.

(20) Schmidt, R.; Tanielian, C.; Dunsbach, R.; Wolff, C. *J. Photochem. Photobiol. A.: Chem.* **1994**, *79*, 11.

(21) Weast, R. C.; Astle, M. J. *CRC Handbook of Chemistry and Physics;* CRC Press: Boca Raton, FL, 1996.

(22) Föll, R. E.; Kramer, H. E. A.; Steiner, U. E. *J. Phys. Chem.* **1990**, *94*, 2476.

(23) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems;* Marcel Dekker: New York, 1970.

(24) Sasaki, K.; Kitani, A.; Tsuboi, M. *Nippon Kagaku Kaishi* **1973**, *12*, 2269.

(25) Vedeneyev, V. I.; Gurvich, L. V.; Kondraty′ev, V. N.; Medvedev, V. A.; Frankevich, Ye. L. *Bond Energies, Ionization Potentials and Electron Affinities*; St. Martin Press: New York, 1966.

(26) Bilski, P.; Holt, R. N.; Chignell, C. F. *J. Photochem. Photobiol. A.: Chem.* **1997**, *109*, 243.

(27) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data Suppl.* **1977**, *6*, 1.

(28) Wilkinson, F.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1995**, *24*, 663.

(29) Strickler, S. J.; Berg, R. A. *J. Chem. Phys.* **1962**, *37*, 814.

(30) Wessels, J. M.; Rodgers, M. A. J. *J. Phys. Chem.* **1995**, *99*, 17586.

(31) Böttcher, C. J. F. *Theory of electric polarization*; Elsevier Scientific Publishing Company: Amsterdam, 1973; Vol. 1.

(32) Atkins, P. W.; *Physical Chemistry*, 5th ed.; W. H. Freeman and Company: New York, 1994.

(33) Herzberg, G. *Molecular Spectra and Molecular Structure*; D. Van Nostrand Company: New York, 1950; Vol. 1.

(34) Schmidt, R. *J. Phys. Chem.* **1996**, *100*, 8049.

(35) Minaev, B. F. *J. Mol. Struct. (THEOCHEM)* **1989**, *183*, 207.

(36) Minaev, B. F.; Lunell, S.; Kobzev, G. I. *J. Mol. Struct. (THEOCHEM)* **1993**, *284*, 1.

(37) Schmidt, R.; Bodesheim, M. *J. Phys. Chem.* **1995**, *99*, 15919.