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Quenching of Triplet States by Inorganic Ions. Energy Transfer and Charge Transfer Mechanisms

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Abstract: The effect of inorganic anions on the triplet states of aromatic hydrocarbons and carbonyl compounds (M) in aqueous solution at room temperature was investigated using the fast-reaction techniques of flash and laser photolysis. The results have been interpreted on the basis of two major quenching mechanisms: energy transfer and charge transfer. Typical T-T energy transfer was demonstrated for NO_2^-. Its triplet energy was also determined and found to be $E_T = 53 \pm 2$ kcal/mol. The very fast quenching of triplet acetone by NCS^- may also involve energy transfer. In other cases, the quenching rate constant k_q was found to depend largely on the proximity of the CT level of the M-anion complex to the triplet level of M. The energies of such CT levels were calculated from the thermodynamic properties of the species involved. The dependence of k_q on $\Delta E_{CT} = E_{CT} - E_{M*}$ was examined when M* is either a singlet S_1 or a triplet T_1 excited state. For the systems examined, the analysis reveals that S_1 and T_1 states are quenched by inorganic ions via similar mechanisms, and in both cases k_q becomes diffusion-controlled when $\Delta E_{CT} \lesssim 0$. However, with the exception of SO_3^{2-}, no chemical reactions were found to result from the quenching reaction. Possible reasons for this behavior are discussed. In some of the systems where quenching was slow, minor reactions did take place and could be ascribed to redox interactions with radical ions (or their hydrolysis products) produced from the photoionization of the aromatic molecules, and not to a direct reaction of the ions with the triplet states. Evidence for such a photoionization was provided in a detailed study of naphthalene photolysis in water, and its mechanism is discussed.

I. Introduction

Quenching of excited singlet states by simple diamagnetic anions has been studied extensively through fluorescence measurements, and various mechanisms have been proposed.[2-6] Little is known, however, on the corresponding quenching of triplet states, and it was even concluded that diamagnetic ions hardly have any effect.[7] Some early indications, however, bear evidence to the opposite, e.g., a work[8] on the quenching of fluorescein type dyes with I^-. More recently this problem was studied for anthraquinone triplets by flash photolysis[9] and very efficient quenching by anions was reported involving, in some cases, net electron transfer reactions with the formation of inorganic radicals and the semiquinone. There is new evidence[10] that these results may be incorrect and that the transient species studied were not the triplets. Recently, the quenching of triplet pyrazine by inorganic anions has been investigated by laser photolysis.[11]

From their studies on triplet quenching by transition metal ions and their complexes, Linschitz et al.[12] reached the following conclusions: (a) diamagnetic ions can act as efficient quenchers; (b) there is no essential difference in mechanism between the quenching of excited singlets and triplets; (c) charge transfer states appear to play an important role. For the quenching and photoreduction of carbonyl triplets by amines this role is now reasonably well established,[13] but with simple anions as quenchers the picture is unclear even in the case of singlet quenching. In his recent works[5b,6] Watkins has presented serious arguments against the charge transfer mechanism although he still emphasizes the role of some kind of coupling with CT states. He also investigated the quenching of biphenyl, naphthalene, and anthracene triplets by I^-, NCS^-,

Br^-, and NO_3^-, and found it to be relatively slow and unrelated to the redox properties of the systems.[5b] It was argued that coupling to CT levels is no longer important for triplet quenching, because of the relatively large energy separation from triplet levels.[5b]

The purpose of this work is to derive some systematic information on the quenching of triplets by inorganic anions as a basis for examining various possible mechanisms. This study is also directly relevant to the general problem of intersystem crossing paths,[14] and to the difference in the quenching mechanism between singlets and triplets. The results of this work also provide information on: (a) The triplet states of inorganic anions on which little is known. The available information has been acquired by absorption and emission spectroscopy.[15] An energy transfer method was used[16] for SO_3^{2-}, but the conclusions drawn are questionable (see section IIID). Similar methods have recently found considerable use in inorganic photochemistry, e.g., of coordination compounds.[17] (b) The properties of triplets in aqueous solutions, in particular their role in the photoionization of aromatic compounds. For this purpose the photochemistry of naphthalene in water was investigated. The absence of close scrutiny between the reactions of anions with free radicals and those directly involving triplets can lead to wrong conclusions concerning the origin of some redox products in similar systems (see below).

II. Experimental Section

The flash photolysis, pulse radiolysis, and 265-nm laser photolysis setups were described elsewhere.[18] Flash intensity was varied by changing the charging voltage of the capacitors in the range 17–23 kV.[19] Flash duration (1/e) was ~10 μs. The flash photolysis cells were fitted with an outer jacket which contained appropriate filter solution, to avoid appreciable light absorption by the quencher. A 0.1% potassium biphthalate in water with cutoff at ~302 nm was usually used, but solutions of sodium benzoate[19] and acetic acid were also employed. In some experiments, for example with NO_2^- and $Fe(CN)_6^{4-}$ at concentrations higher than 10^{-4} and 10^{-5} M, respectively, some absorption by the anions could not be avoided. Possible complications should be considered, e.g., quenching by reactive intermediates or products such as NO and NO_2 produced from the photolysis of NO_2^- etc.[20] Using these filter solutions and by reducing the concentrations of organic solutes to ca. 10^{-5} M, triplets and radicals were usually kept at low concentrations (10^{-6} to 10^{-7} M). Due to the long optical path (20 cm) and high extinction coefficients of triplets, their absorption was still high; see Figure 1. Nevertheless, in most flash experiments triplet-triplet annihilation could not be avoided and therefore the kinetics had to be computer analyzed in terms of competing first- and second-order kinetics.[21] From plots of first-order rate constants against quencher concentration, the quenching rate constant k_q was determined. For the shorter-lived triplet of acetone, which was studied by laser photolysis, the second-order component could be ignored.

Materials. The naphthyl carbonyl compounds (J. T. Baker, Triplet Sensitizer Grade) were used without further purification. All other materials were of purest grade available commercially. Naphthalene 2-sulfonate and the carbonyl compounds were dissolved in water by shaking or warming up to 60–80 °C. To prepare the hydrocarbon solutions, it was first dissolved in *tert*-butyl alcohol and then diluted with water. Most of these solutions contained 1–5% *tert*-butyl alcohol, but for chrysene and coronene higher concentrations of alcohol were required (~50%). The alcohol rich solutions were more viscous and therefore quenching rate constants were normalized as follows: the diffusion-controlled quenching of naphthalene 2-sulfonate by NO_2^- was determined in water (k_{H_2O}) and in the mixed solvent (k_{mix}) and a k_{H_2O}/k_{mix} was applied as a normalization factor for other quenching reactions in the same solvent.

The concentration of the organic solute present in solution was determined from its optical absorption, using available data on its spectrum in pure alcohol. The quencher at the appropriate concentration was finally added. In all cases the final absorption was measured before irradiation and there was no sign of any chemical interaction between the components in their ground states.

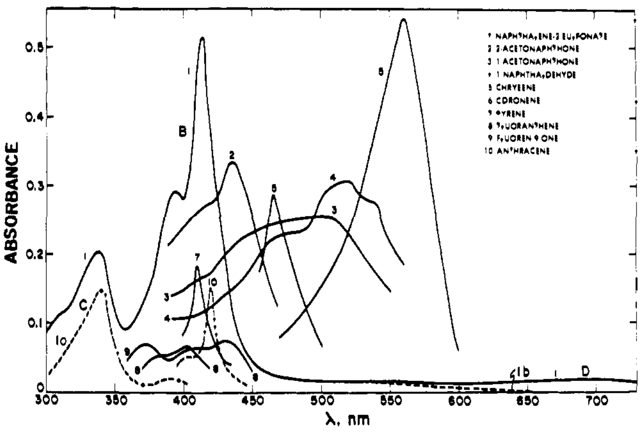

Figure 1. Transient spectra produced on flash photolysis of various aromatic hydrocarbon and carbonyl compounds in air-free aqueous solutions: curve 1 and 1a, 60 μM, pH ~6, measured at ~50 μs and 2 ms, respectively; curve 1b, 60 μM, 2.4 mM $HClO_4$, measured at ~50 μs after the flash. Curve 10, 8.5 μM, pH ~6. All other solutions contained ~10 μM of the organic compounds at pH ~6. (Amount of alcohol in the hydrocarbon solutions—see Experimental Section and Table I.)

III. Results and Discussion

A. Photochemistry of Naphthalene in Water. Events in the nanosecond time scale were studied by laser photolysis. Absorptions produced in ca. 10^{-4} M solutions of naphthalene 2-sulfonate, immediately after the pulse (~4 ns duration), revealed a very short-lived transient A peaking at 425 nm. Its decay was monitored at 450 nm and followed a first-order kinetics with $k = 4.3 \times 10^7\ s^{-1}$.

An emission around 330 nm with the same lifetime was also observed. A much longer-lived transient B, λ_{max} ~410 nm, was found to grow in with almost the same rate (monitored at 405 nm) as the decay of transient A. These results resemble those observed with naphthalene in cyclohexane[22] and accordingly we assign bands A and B to transitions originating from the S_1 and T_1 levels of naphthalene, respectively. The lifetime of S_1 drops from 108 ns in cyclohexane to 45 ns in water.[23] It drops further to 23 ns on conversion of naphthalene to its 2-sulfonate derivative.

For the microsecond time scale, the flash photolysis technique was employed. Figure 1 shows the absorptions produced in air-free solutions, ~50 μs (curve 1) and 2 ms (curve 1a) after the flash. No absorption was observed in the presence of air here and with the other systems studied in this work by flash photolysis. Three different transitions were clearly discerned: (a) A very intense absorption B, λ_{max} ~413 and ~390 nm, that closely resembles that of triplet naphthalene in various solvents,[24] including water.[24d] Its decay rate is considerably increased on raising the concentration of naphthalene 2-sulfonate (N) from 10^{-5} to 2×10^{-4} M. From computer analysis (see Experimental), the competing reactions were found to have: $k_1 = 250 + (5 \times 10^6)\,[N]\ s^{-1}$ and $2k_2/\epsilon_{410} = 2.5 \times 10^5$ cm s^{-1}. The apparent self-quenching by ground state molecules could, in part, be an artifact since radicals are also formed which could contribute to the quenching. (Under the conditions employed the radical concentration was almost proportional to [N]; see below.) Some self-quenching probably also occurs.[25] (b) A longer-lived transient C with λ_{max} 340 nm (Figure 1, curve 1a; the difference in lifetime was very pronounced at $[N] \gtrsim 10^{-4}$ M). In neutral or alkaline solutions, the sharp absorption centered around 340 nm was still growing in and reached its maximum value only ~100 μs after the flash. A similar observation was made with naphthalene in an ethanol-methanol mixture at 113 K,[24a] but the transient was not identified. (c) A relatively weak and fast-decaying absorption D peaking at ~700 nm. Its decay was first order with k = (1.5

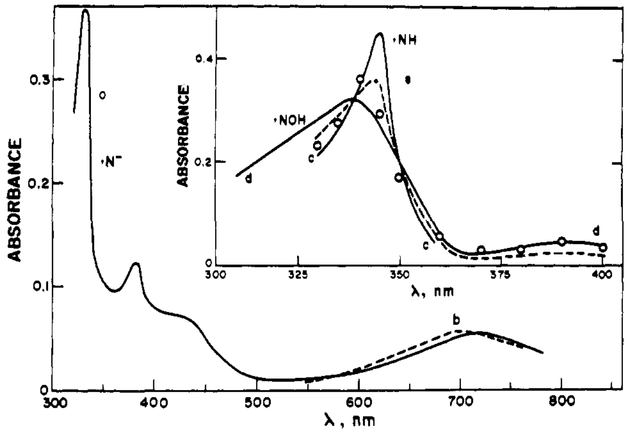

Figure 2. Transient spectra produced by pulse radiolysis of naphthalene 2-sulfonate in aqueous solutions: (a) 1 mM, 1 M *tert*-butyl alcohol, pH 8.5, Ar(1 atm); (b) (dashed) band D, normalized, from Figure 1. Insert: (c) 2 mM, 1.2 M *tert*-butyl alcohol, pH 4.1, Ar(1 atm); (d) 0.1 mM, pH 7, N_2O(1 atm) (multiplied by ½ since N_2O converts e_{aq}^- to OH and $G_{e_{aq}^-} \sim G_{OH}$); (e) (dashed) ½[(c) + (d)]; (circles) band C, normalized, from Figure 1.

$\pm$ 0.5) × 10^4 s^{-1} in neutral solutions, independent of [N] in the range 5 × 10^{-6} to 5 × 10^{-5} M. Similar results were obtained with naphthalene itself. The decay of D and the growth at 340 nm appeared to proceed simultaneously. In acid solutions D was suppressed (Figure 1, curve 1b) and the absorption at 340 nm, while reaching the same value as in neutral solutions, was fully developed during flash duration. D was also removed by adding N_2O or KNO_3 but now with some decrease in the absorption around 340 nm. Evidently there is a close relation between C and D. To determine their nature the pulse radiolysis technique was employed.

Figure 2 shows the transient absorptions produced immediately after the 30-ns electron pulse in 10^{-3} M naphthalene 2-sulfonate at pH 8.5. With Ar-saturated solutions containing 1 M *tert*-butyl alcohol to scavenge OH radicals, a spectrum assigned to N^- (electron adduct) was recorded with maxima at ~710 nm (ϵ 2.6 × 10^3 M^{-1} cm^{-1}), ~440, 380, and 330 (ϵ 1.7 × 10^4 M^{-1} cm^{-1}). It is formed from the reaction $N + e_{aq}^- \rightarrow \cdot N^-$, and its rate was determined, $k = (8 \pm 1) \times 10^9$ M^{-1} s^{-1}. $\cdot N^-$ was found to decay by protonation with $k = 2.2 \times 10^4 + 9 \times 10^9\,[H^+]$ s^{-1}. The first term, which represents protonation by water is somewhat higher than the decay rate of transient D (its spectrum is included in Figure 2 for comparison), but owing to the higher concentration of radicals produced by pulse radiolysis this term may conceal a second-order component. On decaying $\cdot N^-$ was found to be replaced by another absorption below 400 nm, most probably that of the protonated form ·NH (Figure 2, insert), with a sharp maximum at 345 nm, ϵ_{max} 3.2 × 10^4 M^{-1} cm^{-1}. A transient assigned to the OH adduct was also observed by pulse radiolysis of solutions saturated with N_2O: λ_{max} 340 nm, ϵ_{max} 2.3 × 10^4 M^{-1} cm^{-1}. It is shown in Figure 2, insert, together with the spectrum of an equimolar mixture of ·NH and ·NOH (dashed curve). This composite absorption closely resembles the spectrum of transient C, which is reproduced in Figure 2 (insert). Similar results were recently derived for pulse radiolysis of naphthalene in aqueous micellar solutions,[26] except for some spectral shifts and in particular a much lower value of ϵ_{max} ·NH.

The production of radicals in the photolysis experiments was found to be suppressed by triplet quenchers even at quencher concentration below 10^{-4} M, when S_1 (τ = 23 ns) could hardly be affected. Effective quenchers were O_2, NO_2^- (see below), and hexadienol. These quenchers may also react with the radicals. We verified by pulse radiolysis that hexadienol does not affect the amount or decay of ·NH radicals under our experimental conditions.

These findings convince us that naphthalene undergoes photoionization in solution to produce both positive and negative ions, and that the triplets or their precursors are involved but not S_1. $\cdot N^+$ is very rapidly hydrolyzed to form the OH adduct, while protonation of $\cdot N^-$ by water is relatively much slower. To elucidate the mechanism, the effect of light intensity (I) was studied. The absorption at 340 nm was found to increase with I^2 which suggest a biphotonic process while the triplet yield was almost proportional to I. Ionization by triplet–triplet annihilation, as in tetrahydrofuran solutions,[27] can be ruled out since (a) the generation of radicals is complete within the flash duration (in acid solutions); (b) by keeping the light energy constant and varying [N], the triplet yield could be considerably varied but the ratio R = radical yield/triplet yield remained constant; (c) the effect of N_2O and NO_3^-, which are electron scavengers, suggests that ionization proceeds as follows:

$$N + h\nu \rightarrow \cdot N^+ + e_{aq}^-,\ e_{aq}^- + N \rightarrow \cdot N^-$$

probably via a triplet which absorbs another photon. However, the triplet role is still questionable, since we were unable to change R by using a $NiSO_4 + CoSO_4$ filter which removes most of the light absorbed by the 413-nm triplet band.

The following anions were found to have no appreciable effect on the decay rate of the naphthalene 2-sulfonate triplet up to 10^{-2} M: Cl^-, Br^-, I^-, NCS^-, NO_3^-, SO_3^{2-}. This puts for them an upper limit, $k_q < 10^4$ M^{-1} s^{-1}. However, with Br^-, I^-, NCS^-, and SO_3^{2-} the transient absorption observed was somewhat modified in a way that suggests oxidation of these anions by the radical ion $\cdot N^+$ (or ·NOH). With Br^-, I^-, and NCS^-, there was a decrease in absorption below ~350 nm and a small increase around 360, 380, and 480 nm, where Br_2^-, I_2^-, and $(NCS)_2^-$, respectively, display their maxima.[28] With SO_3^{2-} only the decrease was noticed since SO_3^- absorbs appreciably only below 300 nm.[29] These observations suggest that the possibility of reactions of inorganic anions with radicals must be considered when an attempt is made to relate redox reactions to direct interactions with excited states (see later)

Among the anions that we examined only $Fe(CN)_6^{4-}$ and, in particular, NO_2^- were found to quench the triplets effectively (Table I). $[Fe(CN)_6^{4-}] > 10^{-4}$ M was used in these experiments and therefore there is some uncertainty in this case (see Experimental Section); but there is no doubt that NO_2^- quenches triplet naphthalene very fast, with almost diffusion-controlled rate.

B. Quenching of Triplets by NO_2^-—The Energy Transfer Mechanism. The striking effect of NO_2^-, compared to other anions, on the quenching of triplet naphthalene cannot be explained in terms of its redox properties (see later) or heavy atom effect and therefore suggests an energy transfer mechanism. This view was verified by examining the effect of NO_2^- on other organic triplets, with energy E_T which varied in the range 42–78 kcal/mol. The absorption spectra of these triplets in water, except for acetone, are shown in Figure 1. They were all quenched by NO_2^- with rate constants that varied sharply with E_T in the range 50–60 kcal/mol (Table I). Below $k = 10^7$ M^{-1} s^{-1} the data should be considered as upper limits since relatively high concentrations of NO_2^- had to be used; see Experimental Section. The "titration curve" displayed by plotting log k_q against E_T (Figure 3), is typical for energy transfer[30] and yields $E_T(NO_2^-) = 53 \pm 2$ kcal/mol. This is in good agreement with the value ~57 kcal/mol estimated from absorption and emission spectra, where the 0-0 transition could not be identified.[15a]

The question arises as to the fate of triplet NO_2^-. The photolysis of NO_2^- was shown[20] to lead to the primary disso-

Table I. Second-Order Rate Constants ($M^{-1}\ s^{-1}$) for Quenching of Triplets by Inorganic Anions and Their Redox Properties

Triplet M	NO_2^-	$Fe(CN)_6^{4-}$	$NCSe^-$	I^-	$S_2O_3^{2-}$	SO_3^{2-}	N_3^-	Br^-	NCS^-	NO_3^-	Cl^-	$E_{1/2} + E_T$ eV[g]
Fluorenone	4.9×10^7			$>10^8$	1.4×10^9		1.1×10^9	$\leq 10^5$	$\leq 10^5$			1.25
Acetone	3.0×10^9		6.3×10^9	7.1×10^9	1.7×10^9	*d*	3.5×10^8	5.5×10^6	2.0×10^9	$<10^5$	$<10^4$	1.20
1-Naphthaldehyde	1.6×10^9	4.0×10^9	1.1×10^9	2.8×10^8	3.6×10^7		2.4×10^7	$\leq 3 \times 10^3$	*e*			1.10
2-Acetonaphthone	3.2×10^9	3.0×10^9	4.8×10^7	1.4×10^7	2.4×10^6	*d*	1.2×10^6	2×10^4	1.5×10^4			1.10
1-Acetonaphthone	2.4×10^9	2.7×10^9	1.0×10^7	3.7×10^6	5.2×10^5	*d*	2.0×10^5	*e*	$\leq 10^3$			1.02
Fluoranthene	3.5×10^8			$<10^4$ [c]								0.53
Coronene	5.0×10^8 [a]											0.36
Chrysene	1.0×10^9 [b]	3.5×10^7 [b]										0.18
Naphthalene 2-sulfonate	2.0×10^9	1.4×10^7		$<10^4$		$<10^4$	$<10^4$	$<10^4$	$<10^3$	$<10^4$	$<10^4$	0.07
Pyrene	4.0×10^6			$<10^4$ [c]								0.01
Anthracene	1.0×10^6											−0.13
E_X(sol), eV[f]	5.45			5.65			5.75	6.50	6.53	6.80	7.05	
$h\nu$(CTTS), eV[f]	6.45	4.84	5.27	5.48	5.77		~6.1	6.25	5.57		7.1	

[a] 40% isopropyl alcohol. [b] 46% *tert*-butyl alcohol. [c] Increased triplet formation. [d] Faster triplet decay but strong overlap with spectrum of products. [e] No distinct effect on triplet decay, minor changes in transient spectrum and kinetics. [f] From Table II. [g] See Table III.

ciation reaction:

$$NO_2^- \rightarrow NO + O^- \qquad (1)$$

If reaction 1 occurs via the triplet state of NO_2^- then energy transfer from, e.g., naphthalene to NO_2^-, should lead to the production of OH radicals. The latter could be detected by their reaction with naphthalene to form the OH adduct or with OH scavengers such as Br^- to form Br_2^-. No evidence could be found for these reactions under conditions where most of the OH radicals, if formed, would have reacted with naphthalene or Br^-. This suggests that reaction 1 requires more than 53 kcal/mol and that the photolysis of NO_2^- does not proceed through triplets. Furthermore, our attempt to observe by laser photolysis of NO_2^- optically excited at 265 nm an absorption that could be assigned to the triplet-triplet transition failed.

Apart from NO_2^- and perhaps $Fe(CN)_6^{4-}$ (examined with naphthalene 2-sulfonate and chrysene, Table I), all the other anions had little effect on the decay of the triplets of other aromatic hydrocarbons, namely, on the intersystem crossing $T_1 \rightarrow S_0$. Triplet-triplet energy transfer to $Fe(CN)_6^{4-}$ can also take place, since the T_1 state assigned to it has relatively low energy.[17a] However, with relatively long-lived excited singlets S_1, such as that of pyrene and fluoranthene,[7] a considerable enhancement of the triplet in the presence of I^- was observed, i.e., an enhancement of $S_1 \rightarrow T_1$ intersystem crossing.

C. Quenching of Carbonyl Triplets. The Charge Transfer Mechanism. A completely different picture was exhibited by carbonyl compounds. Flash photolysis of the aromatic carbonyl compounds in water revealed two distinct transient species (Figure 1): one which resembles the triplet absorption as recorded in other solvents[31,7] and the other, much longer lived, which closely resembles that of the ketyl radicals.[32] The long-lived absorptions are shown in part in Figure 1 as tails to the main bands which they considerably overlap. They were not studied in detail but were examined to determine any effect due to the addition of quenchers. (Long-lived transients were also produced from all the aromatic hydrocarbons we studied. They are probably due to radical ions or their hydrolysis products, as in the case of naphthalene; see Section IIIA above.)

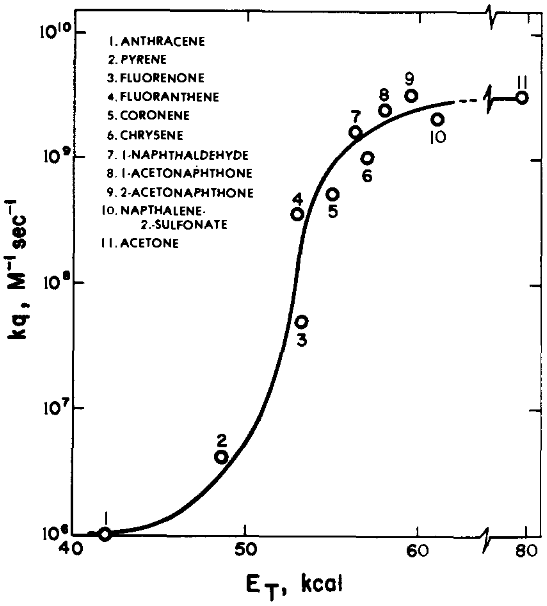

Figure 3. The effect of triplet energy on the rate constant of quenching by NO_2^-.

The carbonyl triplets are generally much more susceptible to quenching by anions than the aromatic hydrocarbons; see Table I but notice the exception of NO_2^-. The quenching rate constants reveal a very large variation in effectiveness, depending on both the nature of the quencher and of the triplet. With slight deviations, all the systems examined followed the same pattern of quenching (For NCS^- and SO_3^{2-} see below.)

$$Fe(CN)_6^{4-} > NCSe^- > I^- > S_2O_3^{2-} > N_3^- > Br^- > (Cl^-, NO_3^-) \qquad (2)$$

$$\text{fluorenone} \gtrsim \text{acetone} > \text{1-naphthaldehyde} > \text{2-acetonaphthone} > \text{1-acetonaphthone} \gg \text{hydrocarbons} \qquad (3)$$

In most cases we found no evidence for chemical reactions which might result from quenching, in particular no evidence for induced formation of ketyl radicals or inorganic radicals (e.g., I_2^- or $(NCS)_2^-$ formed from $I + I^-$ or $NCS + NCS^-$, respectively). In some flash photolysis experiments the transient absorption was completely removed by the quencher; i.e.,

Table II. Thermodynamic Properties of Anions X^- and Radicals X and CTTS Transition Energies (kcal/mol)

X^-	$\Delta H_f^\circ(X,g)$[a]	$-\Delta H_f^\circ(X^-,aq)$[d]	L_{X^-}[g]	E_X[j]	$E_X + L_{X^-}$	L_X[l]	$E_X(sol)$	$h\nu_{X^-}$(CTTS)[o]
F^-	18.9	78.7	113	78	193	0.8	192	
Cl^-	28.9	40.0	81	83.5	165	2.9	162	163
Br^-	26.7	28.9	78	77.3	153	3.6	149	144
I^-	25.6	13.4	64	70.5	135	4.6	130	126
OH^-	9.4	55.0	16	42.1	159	6.2	153	152
SH^-	32	4.2	78[h]	53.3	132	~4	128	124
CN^-	111 ± 5	−36.1	78	88	169	2.8	166	
ClO^-	24.2	26.2[e]		67[k]	146	3[m]	143	
NCS^-	77[b]	−17.2	70[h]	81[b]	154	~4	150	129 (154)
NCO^-	16.5[b]	33.5	89[h]	≥60	146	~4	142	147
N_3^-	104[c]	−65.5[f]	66[i]	70 ± 3[c]	136	~4	132	~140
NO_2^-	7.9	25.4	73	55	129	3.6	125	149
ClO_2^-	25.0	16.5		79[k]	138	7[m]	131	~(136)[n]
NO_3^-	17 ± 5	49.4	68	89.5	160	3.9	156	
ClO_3^-	37[d]	23.5	65[h]	91[k]	156	~4	152	
ClO_4^-		31.4	48[i]	134[k]	182	~4	~178	

Unless otherwise states the data were collected from: [a] *"Janaf Thermochemical Tables"*, U.S. National Bureau of Standards, 1965, 1966, 1967; [b] J. G. Dillard and J. L. Franklin, *J. Chem. Phys.*, **48**, 2353 (1968); [c] H. P. Dixon, H. D. B. Jenkins, and T. C. Waddington, *Chem. Phys. Lett.*, **10**, 600 (1971); [d] "Selected Vaues of Chemical Thermodynamics Properties", U.S. National Bureau of Standards, 1952; [e] J. E. McDonald and J. W. Cobble, *J. Phys. Chem.*, **65**, 2014 (1961); [f] P. Gray and T. C. Waddington, *Proc. R. Soc. London, Ser. A*, **235**, 106 (1956); [g] P. Kebarle in "Modern Aspects of Electrochemistry", B. E. Conway and J. O. Bockris, Ed., Plenum Press, Vol. 9, New York, N.Y., 1974, p 1; [h] P. Vasilev et al. *Russ. J. Phys. Chem.*, **34**, 840 (1960) (adjusted to $L_{H^+} = 270$ kcal/mol); [i] H. F. Halliwell and S. C. Nyburg, *Trans. Faraday Soc.*, **59**, 1126 (1963) (adjusted to $L_{H^+} = 270$ kcal/mol); [j] J. L. Franklin and P. W. Harland, *Annu. Rev. Phys. Chem.*, **25**, 485 (1974); [k] V. I. Vedeneyev et al., "Bond Energies, Ionization Potentials and Electron Affinities", Edward Arnold, London, 1966; [l] V. M. Berdnikov and N. M. Bazhin, *Russ. J. Phys. Chem.*, **44**, 395 (1970). The approximate values were taken as close to other polyatomic radicals: [m] ref 43; [n] appears as a shoulder, nature undertermined (ref 43); [o] ref 41.

most triplets were quenched with no apparent chemical effect. In this respect the systems containing SO_3^{2-} were clear exceptions (section IIID). There were also other minor spectral changes and apparent changes in kinetics in some systems containing NCS^- and Br^- (Table I). In these cases, quenching was slow, and the changes are probably related not to the quenching process but to secondary reactions of organic radicals with these anions, which were present in relatively high concentrations (see section IIIA). One may argue that, in some cases, the absorption of the radicals is much weaker than that of the triplets and, therefore, could not have been detected under the conditions employed. Available information on the ϵ_{max} of T-T transition in 2-acetonaphthone (1.05×10^4 M^{-1} cm^{-1} in benzene[33]) and acetone (ϵ_{280} 1.25×10^3 M^{-1} cm^{-1} in water[34]), compared with that of, e.g., I_2^- (1.56×10^4 M^{-1} cm^{-1} in water[28]), would seem to rule out this possibility. It is also unlikely that organic and inorganic radicals were formed and in all cases escaped detection due to fast reactions. In some flash photolysis experiments where very fast quenching occurred, the concentrations of all solutes were $\lesssim 10^{-5}$ M and the radicals even if reacting with diffusion-controlled rates should have had lifetimes long enough to be detected. It has also been shown that radical ions of some aromatic hydrocarbons are sufficiently long-lived to enable their detection in the presence of much higher concentrations of anions.[5]

The common pattern of reactivity shown by series 2 and 3 would seem to imply some common mechanism of quenching, and any major deviation would need to be interpreted on the basis of a different mechanism. Such a deviation is clearly shown by NO_2^-, and its behavior has been explained above in terms of a T-T energy transfer mechanism. Another instance is NCS^- which, with the striking exception of acetone, quenches all other triplets rather slowly (comparable in rate with Br^-, see Table I). The triplet energy of NCS^- derived from absorption and emission spectroscopy is ~80 kcal/mol.[15b] This lies close to that of acetone 78 kcal/mol and, therefore, the occurrence of a T-T energy transfer in the acetone-NCS^- system is plausible.

To understand the nature of the quenching reactions responsible for series 2 and 3, one must look for those molecular properties of the triplet and the quencher which follow the same order. This property is clearly not related to the nuclear charge of the heavy atom and so the "heavy atom effect" can be ruled out. A mechanism to be considered is that involving the charge-transfer state $M^-{\cdot}X$, where M^- is a negative organic ion and X is an inorganic radical, e.g., I, N_3, etc.

In Table I, the reduction potentials of triplet molecules M^* are represented by $E_T + E_{1/2}$, where $E_{1/2}$ is the half-wave reduction potential (vs. SCE). For carbonyl compounds the values refer to solutions rich in water at pH ~7. But since the reductions involved are not well defined ($E_{1/2}$ somewhat depends on pH),[35] there is some uncertainty in these cases. $E_{1/2}$ in alkaline solutions was used for carbonyl compounds,[13] but only few values are available and moreover they apply to conditions remote from those prevailing in our experiments: neutral solutions where M^- may be present as its protonated form in the "CT complex" when it reaches thermal equilibrium. $E_{1/2}$ values of the aromatic hydrocarbons were collected from ref 36, and were determined in acetonitrile or dimethylformamide solutions, in some cases with addition of water.

The electron affinity in solution

$$E_X(sol) = E_X + L_{X^-} - L_X$$

was chosen to represent the reducibility of inorganic radicals X, where E_X is the electron affinity of X, and L_{X^-} and L_X are the solvation energies (with positive sign) of X^- and X, respectively. $E_X + L_{X^-}$ was calculated by two methods: (a) from the separate values of E_X and L_{X^-}, and (b) from the relation $E_X + L_{X^-} = \Delta H_f^\circ(X, g) - \Delta H_f^\circ(X^-, aq) + \Delta H_f^\circ(H^+, aq)$ derived from a simple Born-Haber cycle. Presently accepted data were taken, with values for L_{X^-} and $\Delta H_f^\circ(H^+, aq) = 96$ kcal/mol being based on $L_{H^+} = 270$ kcal/mol.[37] Available values of L_X are not very reliable, but they are relatively small. All necessary data for most common mononegative ions are summarized in Table II. The two methods yield close values of $E_X + L_{X^-}$, the average was taken and $E_X(sol)$ is also recorded in Table I.

For systems which follow series 2 and 3, k_q can be seen to

Table III. Calculated Energies of CT Levels for M·X⁻ Pairs, and Experimental Values of Singlet and Triplet Energy Levels and Half-Wave Potentials for M Molecules (in eV)

M	NO_2^-	SH^-	I^-	N_3^-	NCO^-	Br^-	NCS^-	NO_3^-	Cl^-	E_T[a]	E_S[a,b]	$-E_{1/2}$[d]
Fluorescein	1.57	1.70	1.78	1.87	2.31	2.62	2.66	2.92	3.18	2.05	2.39	0.83[e]
Rhodamine-B	1.39	1.52	1.60	1.69	2.13	2.44	2.48	2.74	3.00	1.86	2.14	0.65[e]
Pyrazine	1.61	1.74	1.82	1.91	2.35	2.66	2.70	2.96	3.22	3.25		0.87[f]
Fluorenone	1.81	1.94	2.02	2.11	2.55	2.86	2.90	3.16	3.42	2.32		1.07[g]
Acetone	2.94	3.07	3.15	3.24	3.68	3.99	4.03	4.29	4.55	3.40	~4.0[c]	2.2[g]
1-Naphthaldehyde	2.09	2.22	2.30	2.39	2.83	3.14	3.18	3.44	3.70	2.45		1.35
2-Acetonaphthone	2.23	2.36	2.44	2.53	2.97	3.28	3.32	3.58	3.84	2.59		1.49[h]
1-Acetonaphthone	2.24	2.37	2.45	2.54	2.98	3.29	3.33	3.59	3.85	2.52	1.50[h]	
Fluoranthene	2.51	2.64	2.72	2.81	3.25	3.56	3.60	3.86	4.12	2.30	3.14	1.77
Coronene	2.78	2.91	2.99	3.08	3.52	3.83	3.87	4.13	4.39	2.40	2.96	2.04
Chrysene	3.04	3.17	3.25	3.34	3.78	4.09	4.13	4.39	4.65	2.48	3.44	2.30
Naphthalene	3.32	3.45	3.53	3.62	4.06	4.37	4.41	4.67	4.93	2.65	4.0	2.58
Pyrene	2.85	2.98	3.06	3.15	3.59	3.90	3.94	4.20	4.46	2.12	3.33	2.11
Anthracene	2.70	2.83	2.91	3.00	3.44	3.75	3.79	4.05	4.31	1.83	3.31	1.96

Unless otherwise stated the experimental data were collected from: [a] P. S. Engel and B. M. Monroe, *Adv. Photochem.*, **8**, 245 (1971); [b] ref 7; [c] a blue shift in water of +0.2 eV was assumed, as that of the peak; [d] ref 35, 36; [e] ref 6; [f] J. Volke, D. Dumanovic, and V. Volkova, *Coll. Czech. Commun.*, **30**, 246 (1965); [g] I. M. Kolthoff and J. Lingane, "Polarography", Vol. II, Interscience, New York, N.Y., 1952; [h] L. Ya. Kheifets, L. I. Dmitrievskaya, and V. D. Bezuglyi, *Elektrokhimiya*, **6**, 830 (1970).

increase with decrease in E_X(sol) and with increase in ($E_T + E_{1/2}$) for the triplet molecules, see Table I, i.e., with increase in the energy of the overall electron transfer process: $X^- + M^* \rightarrow X + M^-$. For a closer analysis we have calculated the energies of the charge-transfer states $M^-{\cdot}X$. Here one has the advantage that no Coulombic interactions are involved, since one partner is neutral and therefore the unknown complex geometry is not a crucial parameter.

Consider the energy cycle:

$$\begin{tikzcd}
M(g) + X^-(g) \arrow[r, "E_X - E_M"'] & M^-(g) + X(g) \arrow[d, "-L_{M^-} - L_X - \lambda_{CT}"] \\
M{\cdot}X^-(sol) \arrow[u, "L_M + L_{X^-} + \lambda_G"] \arrow[r, "E_{CT}"'] & M^-{\cdot}X(sol)
\end{tikzcd} \qquad (4)$$

where $M{\cdot}X^-$(sol) is a collision complex of an anion X^- and an organic molecule M, both solvated in their ground states, and $M^-{\cdot}X$(sol) is the complex in its excited charge transfer state, all at equilibrium configurations. As before, the L and E terms represent solvation energies (with positive signs) and electron affinities, respectively. λ_G and λ_{CT} are the dissociation energies of the complex in its ground and excited states, respectively; λ_{CT} is probably larger because it involves some valence-bond contribution from two unpaired electrons. However, these terms are probably small, owing to the solvation layers which prevent close approach, and they partly cancel each other through the cycle. Assuming that $\lambda_G - \lambda_{CT} \sim 0$, we finally obtain

$$E_{CT} = (E_X + L_{X^-} - L_X) - (E_M + L_{M^-} - L_M) = E_X(\text{sol}) - E_M(\text{sol}) \qquad (5)$$

the terms for M can be related to $E_{1/2}$(M) by expression 6[38]

$$E_{1/2}(M) = E_M + L_{M^-} - L_M - 4.7\ \text{eV} = E_M(\text{sol}) - 4.7\ \text{eV} \qquad (6)$$

which was found to apply in acetonitrile solutions, and is assumed to hold also for aqueous solutions. From Equations 5 and 6:

$$E_{CT} = E_X(\text{sol}) - E_{1/2}(M) - 4.7\ \text{eV} \qquad (7)$$

and E_{CT} can be calculated from data in Table II and available values of $E_{1/2}$(M). Table III summarizes values of E_{CT} for many $M{\cdot}X^-$ pairs (not only for those experimentally examined here), together with energies of M in its S_1 and T_1 states. The values of $E_{1/2}$(M) used for this calculation are also included.

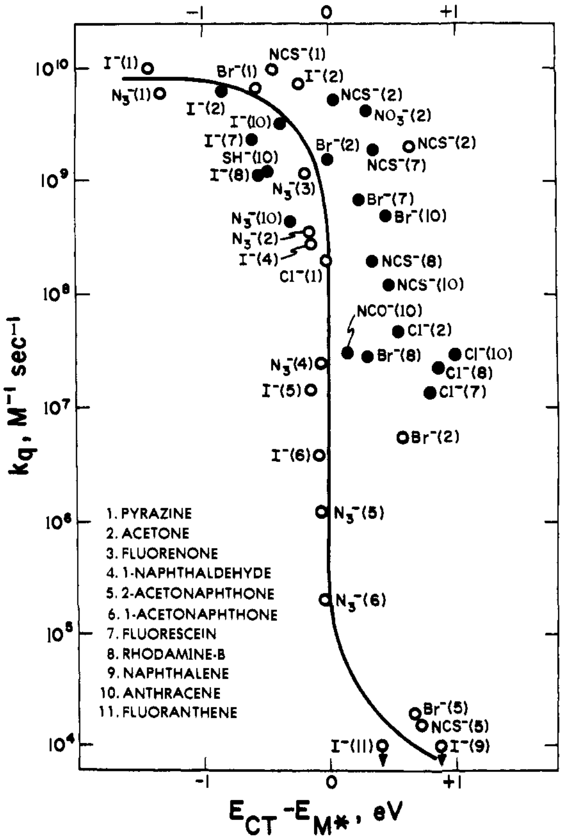

Figure 4. Dependence of quenching rate on the proximity of CT levels to singlet S_1 (●) and triplet T_1 (○) levels. Pyrazine (T), ref 11; acetone (S), ref 3; anthracene (S), ref 2b; fluorescein (S) and rhodamine-B (S), ref 1, with τ = 4.7 and 3.2 ns, respectively (J. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", Academic Press, New York, N.Y., 1971; Landolt-Bornstein, "Luminescence of Organic Substances", New Series, Group II, Vol. 3, 1967).

Table III reveals that $E_{CT} > E_T$ for all the anions and hydrocarbons examined, but the opposite applies to those systems which display fast quenching of the triplet states, namely, aromatic carbonyl compounds, dyes, and pyrazine. The relation between quenching rate constant k_q and the position of the CT level is shown in Figure 4, where log k_q is plotted against $\Delta E_{CT} = E_{CT} - E_{M^*}$, and M* stands either for S_1 or T_1 states. The data for S_1 were collected from various sources, only those involving aqueous solutions were considered (see legend to Figure 4).

Figure 4 shows that the quenching rates of both S_1 and T_1 states fall rapidly below diffusion-controlled level as ΔE_{CT} becomes positive. Most triplets lie on a "titration curve" with $\Delta E_{CT} = 0$ as its "end point". It is important to note that there is no clear distinction between $^3(\pi,\pi^*)$ (e.g., naphthyl carbonyl compounds, fluorenone) and $^3(n,\pi^*)$ (e.g., pyrazine and acetone) states. This is contrary to the higher reactivity shown by $^3(n,\pi^*)$ states, compared to $^3(\pi,\pi^*)$, towards quenching by H-atom donor compounds. This is another piece of evidence that H abstraction does not necessarily occur via an electron-transfer mechanism.[39]

The singlets do show some systematic deviations from the curve, with k_q decreasing more slowly with ΔE_{CT} (Figure 4). However, it should be realized that owing to their much shorter lifetimes, relatively high concentrations of quenchers are required to study k_q below 10^9 M^{-1} s^{-1}. Under these conditions the medium is significantly changed, salting-out and aggregation effects can occur, the excited molecule is under strong electric fields with possible changes in symmetry and electron distribution, and both anions and cations might exert considerable heavy atom effects.

Considerable deviations from the "titration curve" are displayed by systems where energy transfer can take place. This is the case of NO_2^- with triplets having energy levels above ~53 kcal, and probably of NCS^- with the acetone triplet. For clarity the NO_2^- systems were omitted from Figure 4. To cite one example: ΔE_{CT} for the NO_2^- naphthalene pair is +0.67 eV and k_q is 2×10^9 M^{-1} s^{-1}. On the other hand, there is no indication for T–T energy transfer from acetone to NO_3^- (Table I), and therefore $E_{T_1}(NO_3^-)$ is not likely to be ~71 kcal/mol, as previously proposed.[15c] In principle, singlet-singlet energy transfer could occur, e.g., between acetone and NO_3^- [$E(S_1) \sim 4.0$ eV[15c]].[3]

In conclusion, we believe that quenching of singlets and triplets by anions follow similar routes, and the proximity of a CT level provides the most efficient path. Basically the origin of this common mechanism is in the common nature of the quenching process: both involve intersystem crossing. This is self-evident for triplet quenching but it appears to be the case also for singlet quenching.[5] The CT state functions as an effective mediator between the two spin manifolds, most probably because it leads to a certain degree of spin decoupling.

In the equilibrium configuration of the CT state $M^-{\cdot}X$, the solvent is less ordered than in the collision pair $M^*{\cdot}X^-$, because X^- exerts a higher degree of polarization owing to its smaller size, and higher charge when polyvalent anions are considered. Therefore, contrary to the case of donor–acceptor interaction between nonpolar molecules, here we expect a positive ΔS_{CT}; i.e., $\Delta G_{CT} < \Delta E_{CT}$ (no distinction is made here between ΔE and ΔH). Thus we believe that the systems with diffusion-controlled k_q (i.e., $\Delta E_{CT} \lesssim 0$) have negative ΔG_{CT}. Watkins[6] calculated ΔG_{CT} values for some of these systems in CH_3CN and found most of them to be positive. His analysis is based on some previously calculated values of $E(A^-/A)$, the standard reduction potential of the inorganic radical. For water these calculations lead to ΔG_{CT} which is even more positive, contrary to our present calculations.

In agreement with Watkins' findings on singlet quenching,[5b] we found, in most cases, no indication for a net electron transfer reaction in triplet quenching (see above). This important observation has raised[5b,6] the question as to the validity of the charge-transfer mechanism. Since electron transfer appears to be thermodynamically feasible, kinetic barriers must be involved of a nature similar to that treated by Marcus.[40] Complete electron transfer should lead to considerable reorientation of the solvent and may also change molecular geometries. Thus it should proceed through a transition state, which somewhat resembles a charge-transfer-to-solvent (CTTS) state,[41] where the electron is detached from its parent anion but all nuclei still keep their positions as before transfer. Therefore, appreciable activation energy may be required for electron transfer, and k_q may be better correlated with $h\nu_X$(CTTS) than with E_X(sol). Such correlations have already been made for fluorescence quenching.[4] They also have the advantage that anions with unknown E_X(sol) (as $NCSe^-$ and polyvalent anions) can also be included and, indeed, as Table I shows, their positions as quenchers among other anions are in the same order as their $h\nu$(CTTS).

With the exception of NO_2^- and NCS^-, E_X(sol) and $h\nu_X$(CTTS) have relatively close values (Table II).[42] For NO_2^-, however, $h\nu$(CTTS) is much larger than E_{NO_2}(sol), which is probably due to considerable Franck-Condon strain because of the big difference in geometry between NO_2^- and NO_2.[43] In this case, unless effective energy transfer is involved, k_q is much lower than expected from the value of ΔE_{CT}; e.g., for NO_2^- with triplet fluorenone, $\Delta E_{CT} = -0.5$ eV and $k_q = 4.9 \times 10^7$ M^{-1} s^{-1}. For this reason, Figure 3 appears to give an adequate representation of the energy transfer properties of NO_2^- even for the carbonyl compounds. As for NCS^-, the $h\nu_{CTTS}$ is much lower than E_{NCS}(sol), which is difficult to explain. It may raise doubts concerning the identification of its CTTS band, in particular since irradiation of NCS^- at $\lambda > 230$ nm does not yield solvated electrons.[44] The next overlapping band with $h\nu_{max} \sim 154$ kcal/mol,[45] close to E_{NCS}(sol), does yield e_{aq}^-.[44]

From a quantum mechanical point of view, mixing between pure $M{\cdot}X^-$ and $M^-{\cdot}X$ states depends on a Franck-Condon factor, which can be small if the geometries of the relaxed configurations (including solvent) are considerably different. In the systems examined, conditions may prevail when the complex has enough CT character to undergo fast ISC but not enough to make full charge transfer a fast competitive process. This view is in essence similar to that proposed by Watkins[5,6] with the difference that our model implies effective mixing with CT levels only when $\Delta E_{CT} \lesssim 0$. Whether or not this model is valid, the experimental results clearly show an ISC process which does not result from a back-reaction (reverse charge transfer) and thus provide further evidence that in polar solvents spin reversal can be faster than relaxation of the complex, i.e., evidence for the "fast ISC mechanism".[14]

D. Quenching by SO_3^{2-}—Reduction of Triplets. Based on an ESR study, the photolysis of SO_3^{2-} was claimed to be photosensitized by various ketones with triplet energies above 57 kcal/mol.[16] A triplet-triplet energy transfer mechanism was postulated, and for the transfer from acetone ($E_T \simeq 78$ kcal/mol) a rate constant $k_q = 9 \times 10^7$ M^{-1} s^{-1} was determined, which is much less than diffusion-controlled.

By directly following the effect of SO_3^{2-} on some of these triplets we attempted to resolve this problem. In agreement with the ESR work[16] we found that 1- and 2-acetonaphthone triplets are quenched by SO_3^{2-} and ketyl radicals are formed. Because of the strong overlap between the spectra of the triplet and the ketyl radical, k_q could not be determined but appeared to be less than diffusion-controlled. Two possible mechanisms can be offered: (a) a triplet–triplet energy transfer with triplet SO_3^{2-} leading to the formation of e_{aq}^- which subsequently reduces the ketone,[16] or (b) *direct* reduction of the triplet ketone by SO_3^{2-}. Mechanism (a) can be definitely ruled out by our observation that the naphthalene triplet, with higher triplet energy, is not effectively quenched by SO_3^{2-} ($k_q < 10^4$ M^{-1} s^{-1}). Thus the redox properties of the triplet appear to be involved and not merely its triplet energy. So we are left with mechanism (b). The CTTS band of SO_3^{2-} has not been identified. Its absorption above 200 nm does not exhibit CTTS properties although it leads[29] to electron ejection: $SO_3^{2-} + h\nu \rightarrow SO_3^- + e_{aq}^-$. Even if the CTTS band is concealed some-where in this wavelength region its $h\nu_{\max}$ is not likely to be below 130 kcal/mol.[46] Thus with respect to quenching by the charge transfer mechanism, SO_3^{2-} should be less effective than I^-. However, in this case quenching does lead to an overall electron transfer[3] which implies that electron transfer is faster than ISC. The reason for this special behavior is not clear. HSO_3^- is well known to unite with aldehydes and ketones; the possibility of some covalent interaction between their triplets and sulfite should also be considered.

In agreement with the foregoing discussion, SO_3^{2-} quenches acetone triplet[16] slower than I^-, with k_q close to that of N_3^- (Table I). This indicates that triplet-triplet energy transfer from acetone to SO_3^{2-} can hardly be involved, i.e., $E_T(SO_3^{2-}) \geq 80$ kcal/mol. The use of organic triplets to scan this high triplet energy range is limited, because those accessible to measurements have lower E_T values. Inorganic triplets may be used, and some work along these lines has been conducted when studying the effect of OH^- and I^- on the luminescence of Tl^+-doped aqueous halide solutions.[47] The possibility that OH^- and halide ions have relatively low triplet energies[47] is of special theoretical interest since their S_1 states are typical CTTS states where the unpaired electrons are little correlated and therefore low singlet-triplet splitting would have been expected.

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