The Presence of Two Reactive Intermediates in the Photolysis of *N*-Bromosuccinimide: Kinetic Proofs

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The direct photolysis of *N*-bromosuccinimide in the presence of an olefin (to scavenge bromine and its atoms) was shown to produce the ring-opened product β-bromopropionamide from two reactive intermediates as confirmed by kinetic analysis of competing reactions of the ring opening and addition to benzene. The reactive intermediates were assigned to the succinimidyl radical and the precursor in agreement with the previous publication. The plots of relative quantum efficiencies of β-bromopropionamide against benzene concentrations were shown to be consistent with mathematical predictions derived from the proposed reaction scheme. These established that while both the precursor and succinimidyl radical underwent the ring-opening reaction, only the latter showed the reactivity of attacking benzene. The precursor can be either another state of the succinimidyl radical or an excited state of NBS; evidence to distinguish between these is not available. It is surmised that failure to recognize the presence of the precursor in the direct photolysis of *N*-bromosuccinimide has contributed to the protracted controversy in the current literatures.

Introduction

Recently there has been a serious controversy over the number and nature of the radical intermediates involved in the photodecomposition of *N*-bromosuccinimide (NBS) under various conditions.[1-8] Although the claim of generating excited and ground state succinimidyl radicals in thermal propagating reactions has been withdrawn, the presence of another propagating radical intermediate is reiterated in the most recent paper.[3] The detailed chronicle of the controversy including literature citations is described in ref 1 and 3 and will not be repeated here. Viewing the NBS photodecomposition not only as a radical chain process but also as a photochemical process, we have demonstrated that direct photodecomposition of NBS, in the presence of a suitable olefin such as 1,1-dichloroethene (DCE) to scavenge Br_2 and $Br^\bullet$, generated the succinimidyl radical ($S^\bullet$) as well as a precursor, both of which eventually led to the formation of β-bromopropionyl isocyanate (BPI), which was isolated as β-bromopropionamide upon the reaction with water. We employ kinetic studies to prove the presence of two reactive intermediates in photodecompositions of the NBS + DCE system and speculate on the nature of the second reactive species, the "precursor", which has been provisionally regarded[9] as, among other possibilities, a vibrationally excited state of $S^\bullet$. The "precursor" identified in this and previous papers[9] is not related to the so called "third propagating radical" purported to exist in photolysis of NBS and Br_2 mixtures.[3,6,7]

Results

Photolysis of NBS in CH_2Cl_2 in the presence of DCE through a Pyrex filter produced >85% of BPI,[5] but in benzene produced a much smaller yield of BPI.[10] The persistent formation of BPI even in pure benzene was taken as indication that a part of the succinimidyl radical generated under the photolysis conditions ring opened much faster and could not be intercepted by benzene. Therefore, the photodecomposition of the NBS + DCE system was investigated using a Rayonet Reactor (RPR 3000 Å lamps) to photoexcite NBS in the absence and the presence of increasing concentrations of benzene as the competitive scavenger of the reactive intermediates. *N*-Phenylsuccinimide and its tribromocyclohexenyl derivatives had been isolated and characterized in the previous work;[10] in this work the yields of the two compounds were added together to give the total yields of imidation (Table I). Five series of determinations were carried out with a "merry-go-round" placed in a Rayonet Reactor (RPR 3000 Å lamps); irradiation with the 300-nm light source primarily caused the photoexcitation of NBS. As each series was run under identical conditions, the yields of BPI also represented relative quantum efficiencies (ϕ) but not absolute quantum yields (Φ). The yields of *N*-phenylsuccinimide and its tribromo derivatives, therefore, also represented the relative quantum efficiencies of imidation (ϕ_N). Owing to the fact that benzene (B) reacted and its concentrations decreased during the photodecomposition, benzene concentrations lower than 0.03 M should not be used in the present quenching experiments. The plot of ϕ°/ϕ (ratios of the quantum efficiencies of total BPI produced in the absence and presence of benzene) as a function of benzene concentrations for all five series are shown in Figure 1; since the duration of irradiation is cancelled in the ratios, the plot represents that of the absolute quantum yield ratios in the absence and presence of benzene, i.e., $\Phi^\circ/\Phi = \phi^\circ/\phi$. The plot in Figure 1 is an asymptote approaching to Φ°/Φ of about 7.5 at high concentrations of benzene, [B] > 2 M.

The plot is very similar to the quenching of the Type II H-abstraction of 2-propylcyclohexanone by 1,3-pentadiene in which the triplet excited state reaction, but not the singlet excited state reaction, is quenched. Intuitively the asymptote in Figure 1 suggested that a part of total BPI yields could not be quenched even at high benzene concentrations; that is, the total quantum efficiencies of the BPI formation (ϕ or ϕ°) could be defined as a sum of a benzene quenchable term (ϕ_g or ϕ_g°) and an unquenchable term (ϕ_e°) as shown in eq 10 and 11 later. At [B] > 2 M, ϕ_g approached zero and $(\phi^\circ/\phi)_{\text{lim}} = \phi^\circ/\phi_e^\circ = 7.5$ (see eq 15 later). This relation allowed us to calculate ϕ_e° values for each series, and the values of ϕ_g were calculated from

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[1] Tanner, D. D.; Reed, D. W.; Tan, S. L.; Meintzer, C. P.; Walling, C.; Sopchik, A. *J. Am. Chem. Soc.* **1985**, *107*, 6576.

[2] Tanner, D. D.; Meintzer, C. P. *J. Am. Chem. Soc.* **1985**, *107*, 6584.

[3] Skell, P. S.; Lüning, U.; McBain, D. S.; Tanko, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 121.

[4] Days, J. C.; Karsaros, M. G.; Kocher, W. D.; Scott, A. E.; Skell, P. S. *J. Am. Chem. Soc.* **1978**, *100*, 1950.

[5] Tlumak, R. L.; Day, J. C.; Slanga, J. P.; Skell, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 7257.

[6] Tlumak, R. L.; Skell, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 7267.

[7] Skell, P. S.; Day, J. C. *Acc. Chem. Res.* **1978**, *11*, 381.

[8] Walling, C.; El-Taliawi, G. M.; Zhao, C. X. *J. Am. Chem. Soc.* **1983**, *105*, 5119.

[9] Chow, Y. L.; Zhao, D. C. *J. Org. Chem.* **1987**, *52*, 1931.

[10] Lu, F. L.; Naguib, Y. M. A.; Kitandani, M.; Chow, Y. L. *Can. J. Chem.* **1979**, *57*, 1967.

0022-3263/89/1954-0530$01.50/0

Table I. Photodecomposition of NBS in CH_2Cl_2 in the Presence of Benzene[a]

[B], M	products, mmol × 10^3						$k_8\tau_0$, M^{-1} (correlation coefficient)
	BPI[b]	C_6H_5S[c]	$C_6H_6Br_3S$[c]	ϕ_g[d]	ϕ_N	ϕ_e°[e]	
Series I (6 min, *hν*, sign by ■)							
0.00	10.6	-	-	9.19	0.0	1.41	23.2 (0.998)
0.031	7.29	0.73	0.48	5.88	1.21		
0.061	5.54	0.64	0.49	4.13	1.13		
0.15	3.42	0.72	0.62	2.01	1.34		
Series II (8.0 min, *hν*, sign by ×)							
0.00	22.7	-	-	19.7	0.0	3.03	22.1 (0.996)
0.1	8.67	1.38	0.55	5.64	1.93		
0.4	4.66	1.76	0.69	1.63	2.45		
0.8	4.07	2.12	0.65	1.04	2.77		
1.0	3.82	2.94	0.54	0.80	3.47		
Series III (7.6 min, *hν*, sign by ▲)							
0.00	20.0	-	-	17.3	0.0	2.67	20.4 (0.997)
0.1	8.05	1.38	0.52	5.38	1.90		
0.2	6.38	1.83	0.58	3.71	2.41		
0.4	4.41	1.90	0.57	1.74	2.47		
0.6	4.04	2.17	0.60	1.37	2.77		
0.8	3.64	2.17	0.70	0.97	2.77		
1.0	3.43	2.27	0.71	0.76	2.98		
Series IV (8.0 min, *hν*, sign by ●)							
0.0	20.5	-	-	17.8	0.0	2.73	-
1.5	3.22	2.11	0.59	(0.49)	2.70		
2.0	3.37	2.45	0.65	(0.64)	3.10		
2.5	2.83	2.64	0.72	(0.10)	3.36		
3.1	3.25	2.21	0.60	(0.52)	2.81		
5.1	2.56	2.80	0.51	(-)	3.31		
Series V (7.0 min, *hν*, sign by ○)							
0.0	17.0	-	-	14.7	0.0	2.27	-
1.5	2.69	1.97	0.63	(0.42)	2.70		
2.0	3.13	2.01	0.64	(0.86)	2.65		
2.5	3.21	2.30	0.54	(0.94)	2.84		
3.1	3.12	2.18	0.62	(0.85)	2.80		
4.1	2.91	2.22	0.63	(0.64)	2.85		
5.1	2.17	2.26	0.59	(-)	2.85		

[a] For the photolysis and analysis conditions see the Experimental Section; [NBS] = 0.058 M, [DCE] = 0.037 M in CH_2Cl_2 (2 mL). The standard deviations of measured data are about 8%. [b] Since the experiments were run under the conditions for quantum efficiency determination, these figures represent the total quantum efficiency ϕ and ϕ°. [c] The sum of these two figures is ϕ_N. [d] ϕ_g $(=\phi - \phi_e^{\circ})$ and ϕ_g° $(=\phi^{\circ} - \phi_e^{\circ})$; parenthesized figures are expected to contain large error margins. [e] $\phi_e^{\circ} = \phi^{\circ}/7.5$.

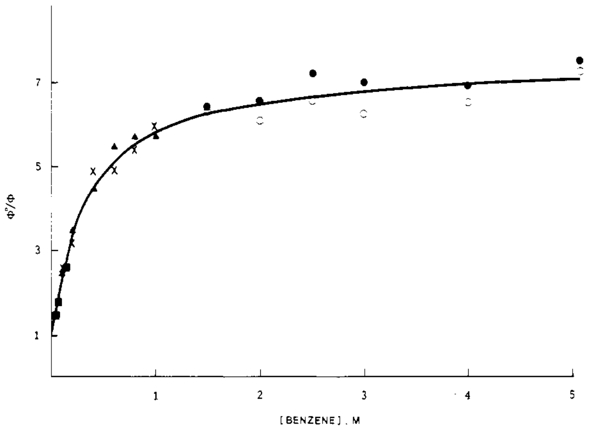


Figure 1. The plot of ϕ°/ϕ (the total quantum efficiency of BPI formations) vs benzene concentration: the curve is drawn according to eq 15 with $\phi_e^{\circ}/\phi_g^{\circ} = {}^{1}/_{6.5}$, $k_8 = 4.2 \times 10^4$ M^{-1} s^{-1}, $\tau_0 = 5 \times 10^{-4}$ s.

the definition $\phi = \phi_g + \phi_e^{\circ}$ as given in Table I. Calculated ϕ_g values in series IV and V contained large error margins because BPI yields were low in the range [B] > 1.0 M. The plot of ϕ_g°/ϕ_g, the ratio of the BPI quantum efficiency quenchable by benzene, against benzene concentrations showed that all the points from the experimental series I–III (Figure 2) could nicely fall into a single correlation giving intercept = 1.01 and slope = 21.2 M^{-1}. It was noteworthy that the straight-line correlation passed the $\phi_g^{\circ}/\phi_g = 1$ at [B] = 0.

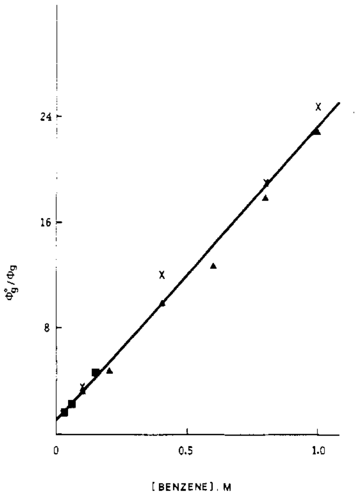


Figure 2. The plot of ϕ_g°/ϕ_g (the quantum efficiency of BPI formations by S·) vs benzene concentration.

The plot of $1/\phi_N$ against 1/[B], another type of Stern–Volmer correlation (see eq 12 later), showed more scatters owing to larger error margins, particularly in the determination of concentrations of the tribromo derivatives as a part of ϕ_N in the low concentration range of benzene.

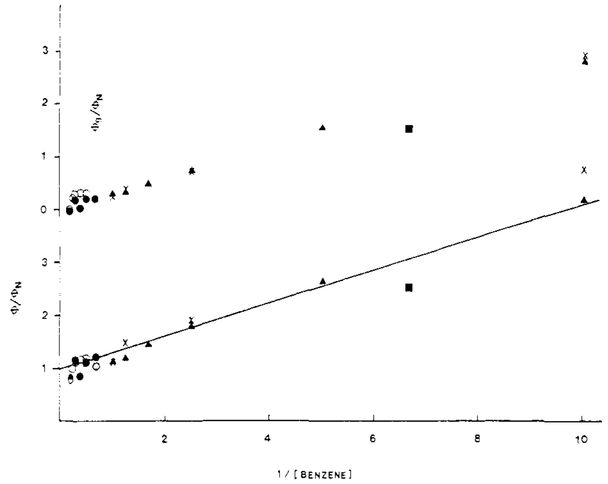
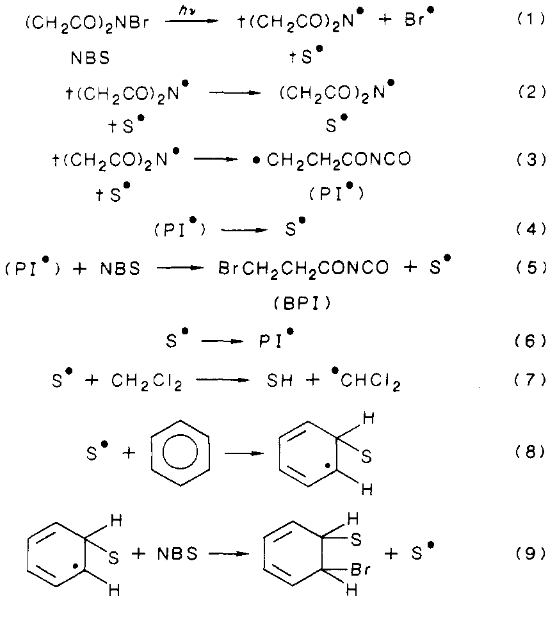


Figure 3. The plot of ϕ_g/ϕ_N (upper) and ϕ/ϕ_N vs 1/[benzene].

While such plots were generally less accurate, the values of the ratio of intercept/slope determined from series II and III were 15 and 18, respectively, and agreed reasonably with those obtained frm the $\phi_g{}^\circ/\phi_g$ plots (Figure 2). The intercepts in these plots do not represent the true value of $1/\varphi_s\lambda_N$ (see eq 12) since ϕ_N values are not the absolute quantum yields. Although ϕ_g values from series IV and V were less accurate, the ratios of ϕ_g/ϕ_N from all series correlated satisfactorily with a single line with a slope of 0.274 passing the origin of the axes as in Figure 3.

Kinetic Analysis. On the basis of the published works, a reaction scheme for the analysis of the photodecomposition of the NBS–DCE system (i.e., in the absence of Br_2) is proposed in eq 1–9. Some assumptions and constraints have to be placed in order to reduce the complex reaction pattern to an essential scheme amenable for kinetic examination involving two reactive intermediates. A direct excitation of NBS generates the precursor of $S^\bullet$ (eq 1) and is temporarily designated as $\dagger S^\bullet$. On the basis of the experimental results presented above, it is assumed that benzene reacts with $S^\bullet$ (eq 8) in competition with the ring opening (eq 6) leading to BPI, but does not react with $\dagger S^\bullet$; that is, the BPI formation from eq 6 is quenchable by benzene (e.g., $\Phi_g{}^\circ$ or Φ_g), but the BPI formation from eq 3 is not (e.g., $\Phi_e{}^\circ$). The ($PI^\bullet$) and (BPI) obtained from $\dagger S^\bullet$ (eq 3 and 5) are not distinguishable experimentally from those derived from $S^\bullet$ (eq 6) but are designated with parentheses for the convenience of mechanistic discussions. The reverse reaction of $PI^\bullet$ gives $S^\bullet$ but not $\dagger S^\bullet$ (eq 4), and its kinetic component is absorbed as part of k_3 and k_6. The quantum yield of $\dagger S^\bullet$ from the photolysis of NBS (eq 1) is assumed to be unity.



Owing to the nature of a chain reaction, the propagation steps (eq 5 and 9) contribute further complications arising from the involvement of NBS concentrations in the regeneration of $S^\bullet$. This complication is alleviated by running the experiments with a fixed initial [NBS] and a low conversion of NBS. The quantum efficiency of the ground state $S^\bullet$ generated from photoexcitation of NBS (φ_s) is assumed to be the same in the absence and in the presence of benzene under the experimental conditions. On the basis of the experimental constraints and assumptions, the total quantum yield of BPI (Φ°) in CH_2Cl_2 (D) in the absence of benzene (B) is defined as the sum of that due to the precursor $\dagger S^\bullet$ ring opening ($\Phi_e{}^\circ$, eq 3) and that due to $S^\bullet$ ring opening ($\Phi_g{}^\circ$, eq 6) as in eq 10. Likewise in the presence of benzene (B), the total quantum yield of BPI (Φ) is the sum of $\Phi_e{}^\circ + \Phi_g$ as in eq 11. The quantum yield of the imidation of benzene (Φ_N) can be expressed by eq 12.

$$\Phi^\circ = \Phi_e{}^\circ + \Phi_g{}^\circ = \frac{k_3}{k_2 + k_3} + \frac{\varphi_s\lambda_b k_6}{k_6 + k_7[D]} \qquad (10)$$

$$\Phi = \Phi_e{}^\circ + \Phi_g = \frac{k_3}{k_2 + k_3} + \frac{\varphi_s\lambda_b k_6}{k_6 + k_7[D] + k_8[B]} \qquad (11)$$

$$\Phi_N = \frac{\varphi_s\lambda_N k_8[B]}{k_6 + k_7[D] + k_8[B]} \qquad (12)$$

In these equations, the repetition cycle of the BPI formation from the ground state $S^\bullet$ is assumed to be λ_b in the absence and the presence of benzene; λ_N represents the cycle of the formation of imidation products. The relation of the ring opening of the ground state $S^\bullet$ with respect to the competing bimolecular reaction of benzene (i.e., the BPI formation quenchable by benzene) can be expressed in eq 13 where $\tau_0 = 1/(k_6 + k_7[D])$, i.e., the lifetime of $S^\bullet$ in the absence of benzene. The slope of the linear plot in Figure 2 is therefore $k_8\tau_0 = 21.2\ M^{-1}$. A similar relation of the total BPI formations, Φ°/Φ, with respect to benzene concentrations is shown in eq 14.

$$\frac{\Phi_g{}^\circ}{\Phi_g} = 1 + k_8\tau_0[B] = \frac{\phi_g{}^\circ}{\phi_g} \qquad (13)$$

$$\frac{\Phi^\circ}{\Phi} = 1 + \frac{k_8\tau_0[B]}{1 + (\Phi_e{}^\circ/\Phi_g{}^\circ)(1 + k_8\tau_0[B])} = \frac{\phi^\circ}{\phi} \qquad (14)$$

$$(\Phi^\circ/\Phi)_{\lim} = 1 + \Phi_g{}^\circ/\Phi_e{}^\circ = (\phi^\circ/\phi)_{\lim} = \phi^\circ/\phi_e{}^\circ \qquad (15)$$

$$\Phi_g/\Phi_N = (k_6\lambda_b)/(\lambda_N k_8[B]) = \phi_g/\phi_N \qquad (16)$$

Equation 14 is further modified to eq 15 in the region of high benzene concentration where the limiting conditions of $1 \ll k_8\tau_0[B] > (\Phi_e{}^\circ/\Phi_g{}^\circ) \times 10^2$ exist. The plot of ϕ°/ϕ ($=\Phi^\circ/\Phi$) exhibits the limiting conditions in the region of [B] > 2 M with $(\phi^\circ/\phi)_{\lim} = \phi^\circ/\phi_e = 7.5$ (Figure 1). Using this value and $k_8\tau_0 = 21.2\ M^{-1}$ from Figure 2, the theoretical asymptote derived from eq 14 was drawn in Figure 1; the agreement of the experimental points with the computer drawn asymptote confirms the reasonableness of the proposed scheme and assumptions; that is, both $S^\bullet$ and the "precursor" decompose to give BPI and the "precusor" cannot be intercepted by benzene. The $\Phi_g{}^\circ/\Phi_e{}^\circ$ value of 6.5 (see eq 15) also indicates that about 13% of the total BPI yield originates from the ring opening reaction of the "precursor" (eq 3), which shows no appreciable reactivity with benzene. The kinetic analysis of thermolysis of NBS in CH_2Cl_2 by Walling's group[8] is the closest to the reactions of the ground state $S^\bullet$ proposed in this work. If $k_6 = 2 \times 10^3\ s^{-1}$ and $k_7 = 1\ M^{-1}\ s^{-1}$ are accepted,[8,11,12] τ_0 at [D] = 15.5 M is calculated to be 5×10^{-4} s: $k_8 = 4.2 \times 10^4\ M^{-1}\ s^{-1}$ is obtained. The contribution from $k_7[D]$ is negligible. The $k_8\tau_0$ values of the individual series were also obtained and listed in Table I.

Discussion

The excellent agreement between experimental data points with the theoretical curve generated on the basis of the proposed reaction scheme as shown in Figure 1 confirms that the precursor does not react with benzene and is much less likely to abstract hydrogen from CH_2Cl_2 or alkanes. This and its propensity to open the ring provide information on its identity. If a succinimidyl radical is considered to be the necessary intermediate for the formation of $PI^\bullet$, the precursor should be another state of $S^\bullet$. Since we have provided reasonable proofs that a related tricyclic succinimidyl radical possesses the Σ electronic configuration by stereoelectronic probes,[13] the precursor could be a succinimidyl radical having the Π electronic configuration. However, the theoretical calculations from many groups[14-17] have been unanimous, with only one exception,[18] in claiming that the Π electronic state is the ground state and lower in energy than the Σ state, which is the excited state of succinimidyl radical. Intuitively, it may be assumed that excited state *NBS decomposes on the same energy surface adiabatically to generate an excited state succinimidyl radical. While it is tempting to assign the precursor †$S^\bullet$ to the lowest excited state as opposed to the assignment of $S^\bullet$ to the ground state succinimidyl radical, the obvious disagreement with the theoreticians' conclusions cautions us that such an assignment is not as straightforward as it appears. If eq 2 involves electronic transition and the energy gap between the ground and excited state succinimidyl radicals is as small as 15–25 kcal/mol as indicated by theoretical studies,[12-14] we would predict high rate constants for k_2 (and, therefore, also for k_3) unless there are orbital symmetry imposed energy barriers. From the fact that benzene fails to quench †$S^\bullet$, we may assume that k_3 is faster than $k_8[B]$ by at least 100 times; it is estimated $k_3 > 4 \times 10^7\ s^{-1}$ by taking [B] = 10.

An alternative explanation is that the precursor is an excited state *NBS, which does not react with benzene but undergoes a simultaneous (or concerted) ring opening to give ($PI^\bullet$) and $Br^\bullet$ during the course of relaxation (eq 3a), bypassing the †$S^\bullet$ formation step; a similar idea has been mentioned by Walling's group[8] and also by us.[9] Equations 1a and 3a substitute eq 1–3 in the mechanistic scheme.

$$\mathrm{NBS} \xrightarrow{h\nu} {}^*\mathrm{NBS} \tag{1a}$$

$$^*\mathrm{NBS} \rightarrow \mathrm{S}^\bullet + \mathrm{Br}^\bullet \tag{2a}$$

$$^*\mathrm{NBS} \rightarrow (\mathrm{PI}^\bullet) + \mathrm{Br}^\bullet \tag{3a}$$

Since there is no proof that the precursor is a radical species, *NBS is evidently just as good a candidate. This mechanistic scheme predicts similar expressions in eq 10, 11, and 14; if $\Phi_e{}^\circ$ is defined as the quantum efficiency of eq 3a, the kinetic analyses described above also apply. As the process in eq 3a must involve two σ-bond scissions by a single photon, it involves the questions of the concertedness of the CH_2–CO and N–Br bond scissions and orbital symmetry correlations. It should be noted if the decomposition of †$S^\bullet$ becomes extremely fast, the identity of the "precursor" becomes indistinguishable between some form of the succinimidyl radical and *NBS. At present, indeed either †$S^\bullet$ or *NBS as the precursor can explain the kinetic results satisfactorily and does not pose mechanistic difficulties.

In the previous publications,[3-8] the so-called relative reactivity (*r* value), which is equivalent to ϕ_g/ϕ_N (or ϕ/ϕ_N), has been used to study kinetics of the complex chain reaction. As shown in Figure 3, a good linear plot of Φ_g/Φ_N against benzene concentrations could be obtained under proper experimental conditions; the slope = 0.274 represents a complex term of $k_6\lambda_b/k_8\lambda_N$. Accepting $k_6 = 2 \times 10^3\ s^{-1}$ and $k_8 = 4.2 \times 10^4\ s^{-1}\ M^{-1}$, $\lambda_b/\lambda_N = 6.0$ is obtained. It is clear that the repetition cycles are important factors in such chain reactions. On the basis of the definition, the plot of ϕ/ϕ_N against the reciprocal of benzene concentrations also should afford a straight line, which should not pass the origin of the axes; this is shown to be the case in Figure 3.

The recent claims that "photodecomposition of NBS in the presence of an olefin involves only the ground state $S^\bullet$" is evidently incorrect;[1,3] if this is the case the plot shown in Figure 1 should give a straight line in analogy to a Stern–Volmer type correlation. It is surmised that the failure to recognize the facile ring-opening reaction of the photolytically generated precursor has indeed brought about misinterpretations of experimental data and has been at least partially responsible for the controversy in the recent years. The yield of BPI is clearly dependent on experimental factors, such as light intensities, fractions of light absorbed by NBS, concentrations of NBS and Br_2, and the wavelength of excitation. Thus, these data from different groups under nonidentical conditions must differ from each other and cannot be compared directly. We hope our results could lead to a reexamination and reconciliation of published data.

Experimental Section

General Conditions and Chemicals. Instruments and their recording conditions, chemicals, and solvents are the same as those described before.[9] *N*-Phenylsuccinimide and its tribromo analogues were prepared as described previously[10] for the purpose of analysis.

Photolysis of NBS in the Presence of Benzene. The preparation of photolysis solutions and degassing followed the procedures describe before.[9] Several methylene chloride solutions containing NBS (0.058 M), DCE (0.037 M), and graded concentration of benzene were degassed in Pyrex tubes (1 × 10 cm) through needles with nitrogen. The tubes were cooled to 15 °C and placed in a rotating platform inside a Rayonet photochemical

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(11) If Walling's rate constants at 50° for $S^\bullet$ ring opening $2 \times 10^4\ s^{-1}$ and that of $S^\bullet$ H abstraction from CH_2Cl_2 6 $M^{-1}\ s^{-1}$ are taken as reasonable values, we estimate that the rate constants at 20–23° may be placed at $k_6 = 2000\ s^{-1}$ and $k_7 = 1\ M^{-1}\ s^{-1}$. In view of the lifetime of 3,3-dimethylglutarimidyl radical of ca. 45 μs at the room temperature in CCl_4 (by flash photolysis),[12] we feel that $k_6 = 2 \times 10^3\ s^{-1}$ is on the lower side. Also, the rate constant of H abstraction from cyclohexane ($3.5 \times 10^3\ M^{-1}\ s^{-}$)[12] may be used for an estimation of $S^\bullet$ reactivities. Since the reactivity ratio (per hydrogen) of succinimidyl radical with cyclohexane and CH_2Cl_2 is ca. 200, $k_7 = 3500/200 \times 6 = 3\ M^{-1}\ s^{-1}$; this estimation seems not too far from Walling's data.

(12) Yip, R. W.; Chow, Y. L.; Beddard, C. *J. Chem. Soc., Chem. Commun.* **1981**, 955.

(13) Chow, Y. L.; Naguib, Y. M. A. *J. Am. Chem. Soc.* **1984**, *106*, 7557.

(14) Clark, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 7746.

(15) Apeloig, Y.; Schrieber, R. J. *J. Am. Chem. Soc.* **1980**, *102*, 6144.

(16) Dewar, M. J. S.; Pakiari, A. H.; Pierini, A. B. *J. Am. Chem. Soc.* **1982**, *104*, 3242.

(17) Dewar, M. J. S.; Olivella, S. *J. Chem. Soc., Chem. Commun.* **1985**, 301.

(18) Kikuchi, O.; Sata, Y.; Suzuki, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2675.

reactor with RPR 3000 Å lamps; during irradiation the temperature inside the chamber did not exceed 20 °C. The sample tubes were irradiated for 6–8 min to cause ca. 15% conversions of NBS.

To the photolysate (1 mL) was added a measured amount of internal standard (3,3-dimethylglutarimide): the residue after evaporation was taken up in $CDCl_3$ (1.5 mL) saturated with water for 400-MHz NMR analysis. The pulsing sequence of the NMR analysis is the same as before,[9] and the intensities of the following signals were utilized to calculate the yields of the products with reference to the internal standard: β-bromopropionamide (BPA), the triplet at 3.65 ppm for $BrCH_2$ protons; succinimide, the singlet at 2.76 ppm for the methylene protons; *N*-phenylsuccinimide, the singlet at 2.91 ppm for the methylene protons; *N*-(tribromocyclohexenyl)succinimide, the singlet at 2.86 ppm for the methylene protons; 3,3-dimethylglutarimide, the singlet at 2.45 ppm for the methylene protons. The control experiments using known concentrations of these products against the standard show that error margins were ±5% when the correct pulsing sequence was used as reported by others.[1,6]

In series I (Table I), experiments with benzene concentrations lower than 0.027 showed nonreproducible results, probably owing to rapidly changing concentrations of benzene.

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Registry No. DCE, 75-35-4; *N*-bromosuccinimide, 128-08-5.

Physical Quenching and Chemical Reaction of Singlet Molecular Oxygen with Azo Dyes[†]

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The quenching rate constants of singlet oxygen lifetime by dialkylamino azo dyes **1** and tautomeric azo dyes **2** and **5** (as well as azo- and hydrazone-model methylated derivatives **3** and **4**) were determined by measuring the 1.27-μm $^1O_2$ emission lifetime, and the values obtained are in the range 10^6–10^8 M^{-1} s^{-1}. The quenching involves a charge-transfer interaction, and different correlations with the oxidation potentials of the two classes of azo dyes are observed. Chemical reactions take place with a rate in the range 10^3–10^4 M^{-1} s^{-1} and are rationalized as a secondary pathway for the charge-transfer complex between $^1O_2$ and the azo dye. Products include dealkylated amino azo dyes **6** from **1**; compounds arising from the fragmentation of the aryl–azo bond, viz., benzenes **7** and phenols **8** from **1** and **2**; and 1,4-naphthoquinone **10** as well as the dimer **9** and the oxidized cyclic derivative **11** from **2**. The methoxy derivative **3** yields an endoperoxide, which rearranges to a 1,2-naphthoquinone derivative **14**. The results are discussed in comparison with the currently accepted mechanism for the reaction of $^1O_2$ with azo dyes.

Introduction

Aromatic azo dyes are presently among the most important dyestuffs for different kinds of applications due to a combination of favorable properties. However, as far as light fastness is concerned, they usually do not rate very high, despite the extremely fast nonradiative deactivation processes characterizing their excited states.[1–4]

The photofading mechanism has been the subject of several investigations. In most cases, a photooxidative fading is observed except for some azo dyes which undergo a reductive photofading[5] when applied onto some textile fibers. The intervention of singlet oxygen, $^1O_2$ ($^1\Delta_g$) has been considered. Thus, bromo-substituted 4-(dialkylamino)-4′-nitroazobenzenes[6] and tautomeric (arylazo)-naphthols have been shown to be able to sensitize the formation of singlet oxygen. The fading of (arylazo)-naphthols due to their reaction with singlet oxygen is believed to be significant,[7] after an important paper by Griffiths.[8] The hydrazone tautomer is thought to be responsible for both singlet oxygen generation and the reaction with singlet oxygen via a diaza analogue of the "ene"[8] reaction. As for azo dyes not subjected to azo–hydrazone tautomerism, their fading is greatly increased in air-equilibrated solutions in the presence of carbonylic compounds.[9,10] The first act of the bleaching process is an electron transfer from the azo dye to the excited ketone or to the radicals formed in the photolysis, depending on

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(1) Kramer, H. E. A. *Chimia* **1986**, *40*, 160 and references therein.
(2) Struve, W. S. *Chem. Phys. Lett.* **1977**, *46*, 15.
(3) Gase, R.; Weber, A.; Grummt, U. W.; Epperlein, J. *J. Prakt. Chem.* **1986**, *328*, 89.
(4) Kobayashi, T.; Degenkolb, E. O.; Rentzepis, P. M. *J. Phys. Chem.* **1979**, *83*, 2431.
(5) Leaver, I. H. In *Photochemistry of Dyed and Pigmented Polymers*; Allen, N. S., McKellar, J. F., Ed.; Applied Science Publishers LTD: London, 1980; p 162–180.
(6) (a) Gruen, H.; Steffen, H.; Schulte-Frohlinde, D. *J. Soc. Dyers Colour.* **1981**, *97*, 430. (b) Görner, H.; Gruen, H.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1980**, *84*, 3031.
(7) (a) Kuramoto, N.; Kitao, T. *Nippon Kagaku Kaishi* **1977**, 258. (b) Kuramoto, N.; Kitao, T. *J. Soc. Dyers Colour.* **1982**, *98*, 334. (c) Merkel, P. B.; Smith, W. F., Jr. *J. Phys. Chem.* **1979**, *83*, 2834. (d) Becker, H. G. O.; Franze, J. *J. Prakt. Chem.* **1981**, *323*, 957. (e) Mustroph, H.; Marx, J.; Epperlein, J. *Acta Polym.* **1983**, *34*, 336. (f) Ball, P.; Nicholls, C. H. *Dyes Pigm.* **1984**, *5*, 437.
(8) (a) Griffiths, J.; Hawkins, C. *J. Chem. Soc., Chem. Commun.* **1972**, 463. (b) Griffiths, J.; Hawkins, C. *J. Chem. Soc., Perkin Trans. 2* **1977**, 747.
(9) (a) van Beek, H. C. A.; Heertjes, P. M.; Schaafsma, K. *J. Soc. Dyers Colour.* **1971**, *87*, 342. (b) van Beek, H. C. A.; Heertjes, P. M.; Schaafsma, K. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 1189.
(10) (a) Albini, A.; Fasani, E.; Pietra, S. *J. Chem. Soc., Perkin Trans. 2* **1986**, 681. (b) The bleaching can be initiated also by the reductive attack of ketyl radicals. See: Flamigni, L.; Monti, S. *J. Phys. Chem.* **1985**, *89*, 3702. Monti, S.; Flamigni, L. *J. Phys. Chem.* **1986**, *90*, 1179.

0022-3263/89/1954-0534$01.50/0