Energetics of Electron-Transfer Reactions of Photoinitiated Polymerization: Dye-Sensitized Fragmentation of *N*-Alkoxypyridinium Salts

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Dedicated to Professor *André M. Braun* on the occasion of his 60th birthday

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Electron transfer from excited dyes to *N*-alkoxypyridinium salts leads to reductive cleavage of the N–O bond to give an alkoxy radical that can be used to initiate polymerization. Bond-dissociation energies obtained from calculations based on density-functional theory are in agreement with predictions from a thermochemical cycle. These data show a difference of *ca.* 290–315 kJ/mol between the BDE of the pyridinium and that of the pyridyl radical and indicate that the fragmentation of the radical is highly exothermic. The energetic requirements for the photochemical electron transfer are discussed in terms of a simplified model that shows that the initiation efficiency of the radical polymerization can be correlated with a single parameter, the reduction potential of the sensitizing dye. Dyes from many classes and with absorption bands spanning the entire visible region were found to be effective in initiating photopolymerization of acrylate monomers in this system. Doubling of the photoresponse can be achieved through coupling of the reductive cleavage of the *N*-alkoxypyridinium with an oxidative cleavage of a C–B bond of an alkyltriarylborate, a process that utilizes the chemical potential stored in the oxidized dye following electron transfer to the pyridinium salt.

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1. Introduction. – In most practical applications of photoinduced radical polymerization, the sensitizers are UV-absorbing compounds that undergo unimolecular fragmentation in an excited state to form the initiating radicals (see, for example, [1]). It has proven difficult to extend this concept very far into the visible region of the spectrum, presumably because the lower bond-dissociation energies required by the lower excitation energies result in compounds with impractical thermal stability. Most of the useful initiating systems that respond to visible light are based on quite different, usually biomolecular, chemistry. For example, a sensitization scheme that has been shown to be useful in the blue region involves a bimolecular electron-transfer reaction between an excited compound (*e.g.*, a ketocoumarin) and an electron donor compound (an amine) to form a radical anion and the radical cation of the amine [2]. Subsequent proton transfer results in radicals that are capable of initiating polymerization [2].

The most promising systems offering further extension of the photoresponse into the visible region are also based on biomolecular electron transfer. However, instead of a proton-transfer reaction that requires the radical ions to have appropriate pK_a values, a fragmentation reaction is used in which the redox-activated reactant leads directly to a free radical [3]. With this approach, the redox potentials of the electron donor and acceptor can be varied to control the chemical reactivity, to allow response to light of

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varying wavelengths, and ultimately allow sensitization by long-wavelength light and low-energy excited states.

The cleavage (fragmentation) reactions can be described as reductive cleavage (*Eqn. 1*) or as oxidative cleavage (*Eqn. 2*), depending on whether the compound that undergoes the cleavage reaction has been initially reduced or oxidized. Here, D* represents an excited state of an electron donor, A* represents an excited state of an electron acceptor, and X–Y is the compound that undergoes cleavage.

Reductive Cleavage

$$D^* + X{-}Y \rightarrow D^{\bullet+} + X{-}Y^{\bullet-} \rightarrow X^{\bullet} + Y^{-} \quad (1)$$

Oxidative Cleavage

$$A^* + X{-}Y \rightarrow A^{\bullet-} + X{-}Y^{\bullet+} \rightarrow X^{\bullet} + Y^{+} \quad (2)$$

The fragmentable X–Y molecule in *Eqn. 1* is neutral and is reduced to a radical anion ($X{-}Y^{\bullet-}$) in the photoinduced electron-transfer step. The radical anion subsequently undergoes bond cleavage to yield a free radical, $X^{\bullet}$, and an anion, Y^{-}. In *Eqn. 2*, the neutral X–Y molecule is oxidized to a radical cation ($X{-}Y^{\bullet+}$), which cleaves to yield a radical and a cation, Y^{+}. The cleavage reactions are expected to be particularly exothermic, and thus favorable, when the radical *and* the ion products are stabilized by appropriate substituents.

When the X–Y molecule is charged, the most likely photoinduced electron-transfer reaction is reduction if the molecule is a cation, and oxidation if the molecule is an anion, to form a neutral radical, $X{-}Y^{\bullet}$. In these cases, fragmentation of the $X{-}Y^{\bullet}$ yields a radical, $X^{\bullet}$, and a neutral species, Y. A number of examples of reductive cleavage of cationic acceptors, $X{-}Y^{+}$ [3][4] (*Eqn. 3*) and oxidative cleavage of anionic donors, $X{-}Y^{-}$ [3][5] (*Eqn. 4*) have been reported.

$$D^* + X{-}Y^{+} \rightarrow D^{\bullet+} + X{-}Y^{\bullet} \rightarrow X^{\bullet} + Y \quad (3)$$

$$A^* + X{-}Y^{-} \rightarrow A^{\bullet-} + X{-}Y^{\bullet} \rightarrow X^{\bullet} + Y \quad (4)$$

These cleavage reactions are expected to be particularly exothermic, and thus favorable, when the species Y is a stable molecule. For example, photoinduced reductive cleavage of diaryliodonium and triarylsulfonium salts is driven by cleavage to form aryliodides and diarylsulfides as the stable Y molecules, respectively [4]. This process is illustrated in *Eqn. 5* for the example of a diaryliodonium compound.

$$D^* + Ar{-}I{-}Ar^{+} \rightarrow D^{\bullet+} + Ar{-}I{-}Ar^{\bullet} \rightarrow Ar^{\bullet} + I{-}Ar \quad (5)$$

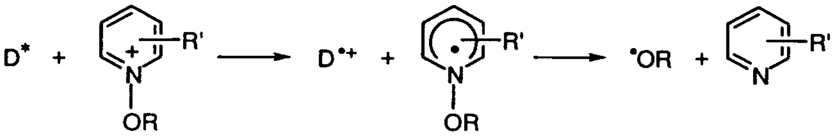
Examples of oxidative cleavage of anions are provided by the reactions of alkyltriaryl borates [5]. The driving force for fragmentation in these cases presumably results from formation of the corresponding stable, neutral triarylboranes (*Eqn. 6*).

$$A^* + R{-}BAr_3^{-} \rightarrow A^{\bullet-} + R{-}BAr_3^{\bullet} \rightarrow R^{\bullet} + BAr_3 \quad (6)$$

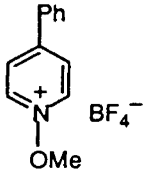
In this paper, we discuss a particularly useful example of such visible-light initiating system that is based on the chemistry of *N*-alkoxypyridinium salts [6]. The emphasis is on a description of the thermodynamics of the photoinduced electron transfer and subsequent fragmentation processes that control the efficiencies of this process, and other such processes in general. Methods for estimating the energetics of the bond-dissociation process are discussed, and a simple method based on a single parameter to predict the efficacy of a sensitizing dye, the reduction potential, is described. Finally, a method based on two fragmentation reactions to double the photochemical efficiency of visible-light-induced polymerizations is described.

2. Results and Discussion. – 2.1. *Reductive Cleavage of* N-*Alkoxypyridinium Salts.* *N*-Alkoxypyridinium salts, the subject of this paper, have been demonstrated as useful sources of radicals for photoinitiated polymerization [6][7]. Single-electron transfer to an *N*-alkoxypyridinium salt results in N–O bond cleavage and the formation of an alkoxy radical, as shown in *Scheme 1* [6][7]. Thus, these reactions represent examples of reductive cleavage.

Scheme 1



The driving force for the fragmentation reaction in this case results from formation of a stable pyridine molecule. The *N*-alkoxypyridinium salts have proven to be effective with a wide range of sensitizers and excitation wavelengths [6]. *N*-Methoxy-4-phenylpyridinium tetrafluoroborate, **A1**, is a particularly useful example of this class of compounds and is discussed in detail here.



A1

The range of useful dyes is determined largely by the reduction potential of the *N*-alkoxypyridinium. As for all compounds that undergo rapid redox activated cleavage, the determination of such potentials is not trivial. A method that seems to be useful for the *N*-alkoxypyridinium compounds is described below.

2.2. *Reduction Potentials.* Reduction of the *N*-alkoxypyridinium salts by cyclic voltametry is irreversible [8] because of fast fragmentation of the N–O bond in the reduced species. Thus, thermodynamically meaningful reduction potentials are not directly accessible for these compounds. Some *N*-alkylpyridinium salts, however, do exhibit reversible electrochemical reduction due to the higher stability of the resultant pyridyl radicals, especially those that are substituted in the 4-position [8]. Because of the stronger *inductive* electron-withdrawing nature of an alkoxy group relative to an alkyl group, *N*-alkoxypyridiniums are expected to be more electron-deficient and thus easier to reduce (*i.e.*, they should have less negative reduction potentials) than the corresponding *N*-alkyl derivatives.

Kochi and co-workers have studied ground-state charge-transfer (CT) complexes of 4-cyano-*N*-methyl- and 4-cyano-*N*-methoxypyridinium salts with several aromatic hydrocarbon compounds as donors [8]. On average, the absorption maxima of the *N*-methylpyridinium CT complexes were observed to be 0.14 V higher in energy than those of the corresponding *N*-methoxy derivatives. The same authors showed that a plot of the CT absorption maximum *vs.* donor oxidation potential had, as expected, a slope near unity. It is, thus, reasonable to conclude that the reduction potential of 4-cyano-*N*-methoxypyridinium is *ca.* 0.14 V less negative than that of the corresponding *N*-methyl derivative.

A similar conclusion was reached by a different approach. The peak potential for reduction of 4-cyano-*N*-methoxypyridinium is -0.30 *vs.* SCE [8]. Based on a rate constant of *ca.* 10^7 s^{-1} for the fragmentation of the resulting radical [9], the standard reduction potential is estimated [10] to be more negative than the peak potential by *ca.* 0.17 V, *i.e.*, $E^{red} \approx -0.47$ V *vs.* SCE. The reversible reduction potential of 4-cyano-*N*-methylpyridinium is -0.64 V *vs.* SCE [8]. Thus, in this case the reduction potential of the *N*-methoxypyridinium salt is less negative than that of the *N*-methyl analogue by 0.17 V, which is close to the estimated increment of 0.14 V mentioned above.

N-Ethyl-4-phenylpyridinium gives a reversible reduction potential of -1.17 V *vs.* SCE. Thus, based on the above discussion, the reduction potential of the *N*-methoxy derivative **A1** is estimated to be -1.0 V *vs.* SCE.

2.3. *Bond-Cleavage Thermodynamics.* Bond cleavage of the *N*-alkoxypyridinium salts leads to formation of a MeO radical and the radical cation of the Py. Bond cleavage of the Py radical formed upon reduction of the salt, however, leads to formation of a MeO radical and *neutral* Py. Clearly, bond cleavage of the Py radical should be more thermodynamically favorable than cleavage of the pyridinium salt. The two cleavage reactions can be related by a thermodynamic cycle [11], as indicated in *Scheme 2* for **A1**. The difference in the bond dissociation energies of the salt, $(BDE)_{A^+}$, and of the radical, $(BDE)_{A^\cdot}$, is given by the difference in the oxidation potentials of the neutral Py, $(E^{ox})_A$, and the Py radical, $(E^{ox})_{A^\cdot}$. The oxidation potential of the radical is equal to the reduction potential of the salt, $(E^{red})_{A^+}$ (*Scheme 2*). The oxidation potential of 4-phenylpyridine is estimated to be *ca.* 2.2 V *vs.* SCE[2]), and the reduction potential of **A1** is estimated to be -1.0 V *vs.* SCE, see above. Thus, the difference between the bond-dissociation energy of the cation and that of the radical in *Scheme 2* is expected to be 3.2×96.5, or 309 kJ/mol.

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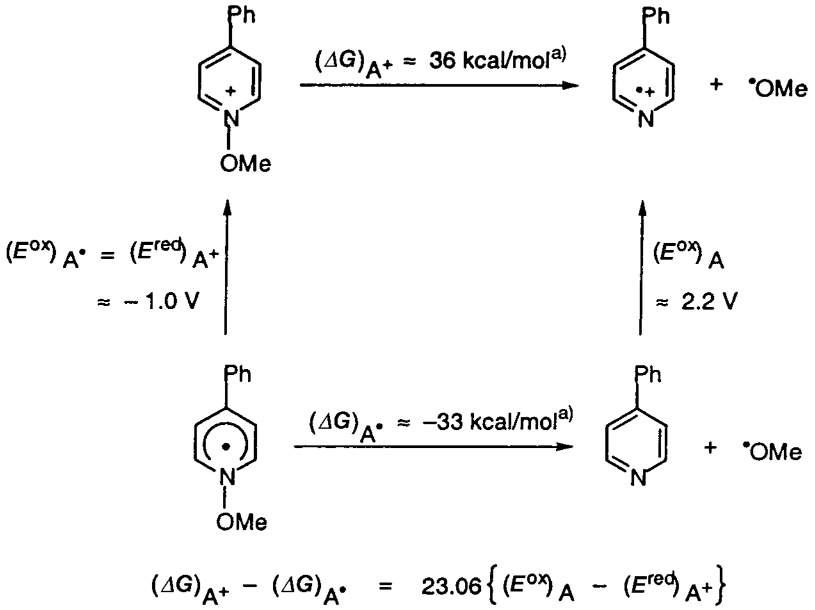
[2]) At a Pt microelectrode by square-wave voltammetry in CH_2Cl_2, 4-phenylpyridine gave an irreversible oxidation peak at 2.23 V *vs.* SCE, which is 0.23 V higher than the oxidation potential of biphenyl measured under the same conditions. This difference in oxidation potential is similar to an average difference of 0.25 ± 0.1 that we observed between a number of related hydrocarbons and the corresponding N-heterocycles (naphthalene/isoquinoline, phenanthrene/phenanthridine, and *trans*-stilbene/2-styrylpyridine).

Scheme 2



a) Including solvent correction for MeCN.

Absolute values for the bond dissociation enthalpies were also calculated by means of density-functional theory. Specifically, the B3LYP/6-311 + G*//B3LYP/6-31G* method [12][13] was used as implemented in the *Gaussian98* package [14]. The gas-phase energies were corrected for solvent effects according to the SM5.4/A solvent model [15] in AMSOL [16], with the recommended parameters for MeCN and the gas phase B3LYP/6-31G* geometries. The bond-dissociation enthalpies calculated in this manner were 230 kJ/mol for the cation and −79 kJ/mol for the radical. Inclusion of corrections for zero-point and thermal energies[3]) gave corrected bond-dissociation enthalpies, ΔH, of 209 and −88 kJ/mol for these species respectively. Adding entropy contributions gave *Gibbs* energy changes, ΔG, for these reactions of 151 and −138 kJ/mol, respectively.

Thus, the difference between the dissociation enthalpies of the pyridinium cation and that of the Py radical, as well as the difference between the *Gibbs* energy changes for these cleavage reactions, are both *ca.* 293 ± 4 kJ/mol. This value is in good agreement with the difference of 309 kJ/mol estimated from the redox potentials, as discussed above. The consistency in energy differences according to the thermochemical cycle of *Scheme 2* provides strong support for a highly negative bond-dissociation energy of the Py radical derived from **A1**. This strongly exothermic cleavage of the N−O bond upon one-electron reduction illustrates the point that redox-induced fragmentation reactions of ionic compounds to generate neutral, stable entities are

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[3]) Corrections were calculated with B3LYP/6-31G* (at 298.15 K, 1 atm, with a scale factor of 0.9806) as recommended in [17].

expected to be quite favorable, and that this is a useful general strategy for generating radicals with high efficiency.

2.4. *Electron-Transfer Energetics.* As illustrated in *Eqn. 7*, dye-sensitized activation of an alkoxypyridinium, $RO-Py^+$, requires electron transfer from the excited state of the sensitizing dye, D^*, to the pyridinium. The reaction products are the oxidized dye (electron donor), $D^{\bullet+}$, and the reactive Py radical, $RO-Py^\bullet$. Clearly, for optimum efficiency, this process should be exothermic.

$$D^* + RO-Py^+ \rightarrow D^{\bullet+}/RO-Py^\bullet \tag{7}$$

The exothermicity of a photoinduced electron-transfer reaction can be calculated as the difference between the energy stored in the excited state, in this case D^*, and that stored in the product electron-transfer geminate pair [18], which in this case is the oxidized dye ($D^{\bullet+}$) and the alkoxypyridyl radical ($RO-Py^\bullet$). For photoinduced electron-transfer reactions between a donor D and an acceptor A, the energy stored in the geminate pair is usually estimated by means of electrochemical properties [18]. The difference between the oxidation potential of D, $(E^{ox})_D$, and the reduction potential of A, $(E^{red})_A$, measured separately in a polar solvent such as MeCN, is referred to as the redox energy, E^{redox}, *Eqn. 8* [18]. In a polar solvent such as MeCN, it has been shown that the energy of a radical cation/radical anion geminate pair is essentially equal to E^{redox} [19].

$$(E^{ox})_D - (E^{red})_A = E^{redox} \tag{8}$$

When the polarity of the medium *decreases*, however, the energy of the geminate pair generally *increases*, so that in low-polarity solvents the energy is higher than E^{redox} by a quantity referred to as Δ [19]. The value of Δ for a radical-ion pair generated by electron transfer between two neutral molecules has been shown to range from essentially zero in MeCN to *ca.* 0.3 eV in a nonpolar solvent such as cyclohexane [19]. The increment Δ has not been determined for reactions between charged molecules, such as those used in the present work, although it is unlikely to be very different. For a photoinduced electron transfer to be exothermic the relationship given in *Eqn. 9* must be satisfied, where $(E^{excit})_D$ is the excitation energy of the dye molecule, and Δ ranges approximately between 0 and 0.3 eV.

$$(E^{excit})_D > (E^{ox})_D - (E^{red})_A + \Delta \tag{9}$$

Although *Eqn. 9* allows fairly accurate determination of the thermodynamic feasibility of reducing an alkoxypyridinium with a sensitizing dye, it requires knowledge of *both* the excitation energy of the dye and its oxidation potential. A simpler, although perhaps less-precise approach makes use of the relationship between the excitation energy of a compound and its oxidation and reduction potentials (indicated in *Eqn. 10* [20].)

$$(E^{excit})_D = (E^{ox})_D - (E^{red})_D + C \tag{10}$$

This relationship was examined experimentally by *Lenhard* for a series of cyanine dyes, who found values for C of 0.25, 0.3 and 0.37 eV for cyanine, carbocyanine, and dicarbocyanine dyes, respectively [20a]. For compounds of quite different structures, *e.g.*, 9,10-dimethoxyanthracene and acridine orange, we found values for C of 0.08 and 0.16 eV, respectively. For asymmetric dyes, such as the four styrylpyridinium compounds given below, we also obtained a C of 0.18 ± 0.02 eV. Thus, although C appears to be somewhat variable and dependent upon the exact structure of the sensitizer, a value of *ca.* 0.25 ± 0.15 eV seems to be quite reasonable. By combining *Eqns. 9* and *10*, the thermodynamic feasibility for sensitized reduction of an alkoxypyridinium can, therefore, be written in terms of the difference between the reduction potential of the sensitizing dye, $(E^{\mathrm{red}})_{\mathrm{D}}$, and that of the alkoxypyridinium acceptor, $(E^{\mathrm{red}})_{\mathrm{RO-Py^+}}$, *Eqn. 11.* From the above discussion, both C (0.25 ± 0.15 eV) and $\varDelta$ (*ca.* 0.2 to 0.3 eV, in medium to low polarity media) are nearly equal in magnitude, and thus $(C - \varDelta)$ should be very small for reactions in such media.

$$(E^{\mathrm{red}})_{\mathrm{D}} - (E^{\mathrm{red}})_{\mathrm{RO-Py^+}} < C - \varDelta \approx 0 \qquad (11)$$

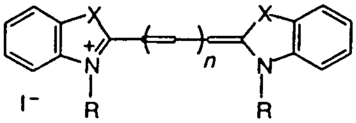
It is clear from *Eqn. 11* that, when the reduction potential of the donor molecule is more negative than that of the alkoxypyridinium (*i.e.*, it is harder to reduce), the photochemical electron transfer reaction will be exothermic. A test of this relationship and its relevance to the efficiency of photoinduced polymerization efficiency is discussed below.

2.5. *Photopolymerization.* As discussed above (*Eqn. 11*), the energetics of electron transfer from an excited dye to an alkoxypyridinium salt, and thus the efficiency of forming initiating radicals, can be estimated simply as the difference in the reduction potentials of the two reactants. The alkoxypyridinium salt that was studied most extensively in our photoinduced polymerization work, was **A1** [6], which has a reduction potential of *ca.* −1 V *vs.* SCE. Accordingly, dyes with reduction potentials equal to or more negative than this value should function as sensitizers for this alkoxypyridinium salt, or at least should be capable of generating initiating radicals.

Evaluation of dye/**A1** combinations with respect to their usefulness as initiating systems for photopolymerization was carried out with an acrylate-based coating formulation (see *Exper. Part*). Irradiation was carried out with a Xe lamp through steps of neutral-density filters that varied in 0.15 units of optical density. The efficiency of photopolymerization was determined by counting the number of retained steps after solvent development, which leaves behind only the areas that had sufficient exposure to cause crosslinking of the multifunctional acrylates. Thus, a more efficient initiator would require less exposure, which corresponds to a higher optical density on the neutral density filter, *i.e.*, a higher number on the step tablet, than a less efficient initiator. Every 2 steps ($\varDelta$ OD = 0.3) correspond to a factor of 2 in polymerization efficiency.

Shown in the *Figure* is a plot of the number of developed steps, as a measure of photoinitiation efficiency, *vs.* reduction potential for a series of dyes. The spectral region covered by these dyes extends throughout the entire visible spectrum. A wide range of dye classes were used, including neutral (*e.g.*, coumarin laser dyes), cationic (*e.g.*, cyanine), anionic (*e.g.*, oxanol), and zwitterionic (*e.g.*, squarylium) dyes (see *Table 1*).

Table 1. *Dyes Used in Photoinitiated Polymerization in Combination with the* N-*Methoxypyridinium Salt* **A1** (λ_{max} in nm, measured in monomer/binder formulation described in *Exper. Part*; E^{red} in V *vs.* SCE; the initiation efficiency is in terms of the number of retained steps after development, see text for details)



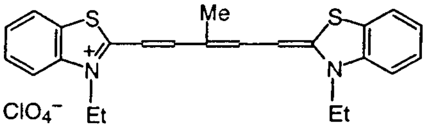
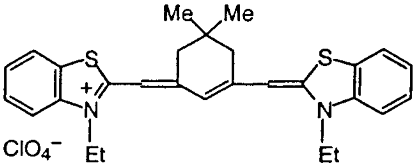
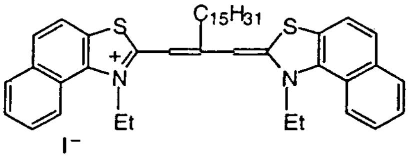
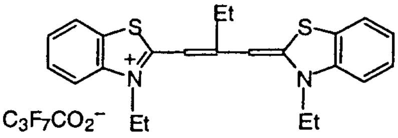
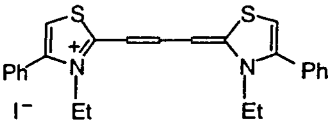
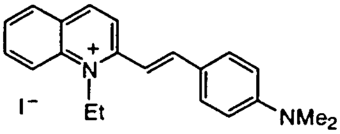
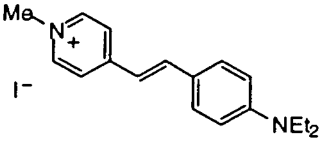
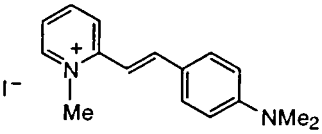
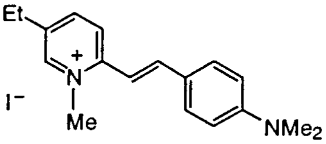
n	X	R	λ_{max}	E^{red}	No. of Steps
3	CMe_2	Me	750	– 0.71	0.5
3	S	Et	782	– 0.78	3.0
2	CMe_2	Me	650	– 0.86	4.0
2	S	Et	670	– 0.93	6.0
1	CMe_2	Me	555	– 1.04	6.0
2	O	Et	595	– 1.09	8.8
1	S	Pr	573	– 1.10	8.5
1	O	Hex	500	– 1.35	10.2
			666	– 0.97	7.0
			663	– 1.02	– 9.0
			592	– 1.12	9.3
			563	– 1.15	10.0
			572	– 1.32	11.0

Table 1 (cont.)

Styrylpyridinium Dyes

	λ_{max}	E^{red}	No. of Steps
	533	– 0.76	7.0
	494	– 1.00	11.5
	468	– 1.03	10.5
	462	– 1.10	11.5

Rhodamine Dyes

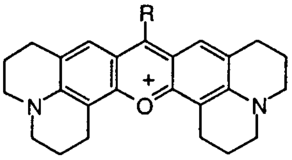
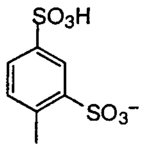
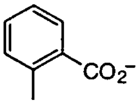
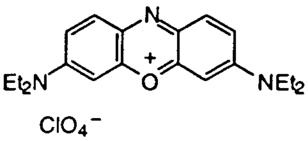
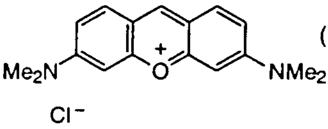
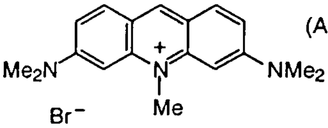
	R	λ_{max}	E^{red}	No. of Steps
Rhodamine 3B		566	– 0.83	2.5
Rhodamine 6G		535	– 0.86	6.0
		592	– 1.05	8.0
		587	– 1.15	8.3

Table 1 (cont.)

Miscellaneous Dyes

	λ_{max}	E^{red}	No. of Steps
 (Oxazine 1)	658	− 0.37	0.0
 (Pyronine Y)	503	− 0.81	4.0
 (Acridine Orange)	503	− 1.13	10.0

Squarylium Dyes

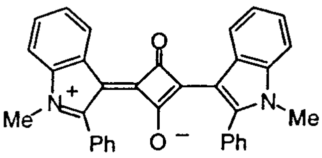
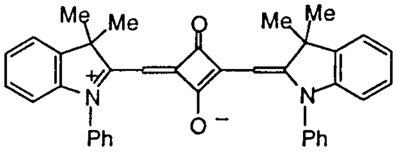
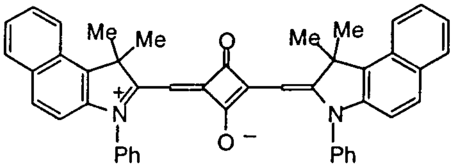
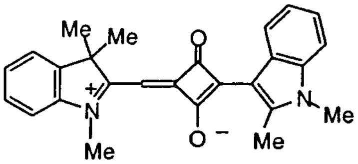
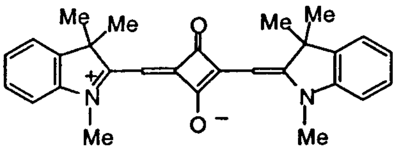
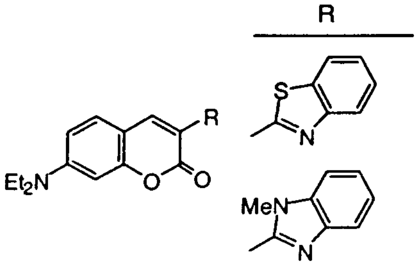
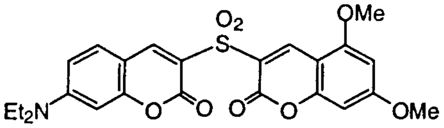
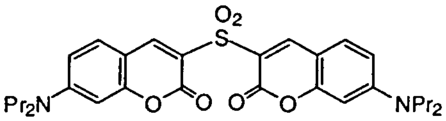
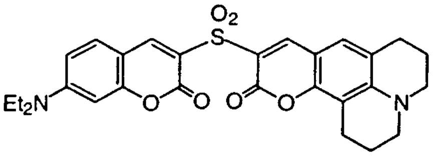
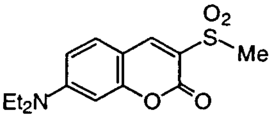
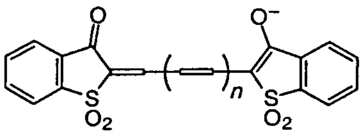
	λ_{max}	E^{red}	No. of Steps
	605	− 0.92	7.1
	652	− 1.02	9.5
	673	− 1.08	9.7
	610	− 1.09	9.5
	642	− 1.18	9.7

Table 1 (cont.)

Coumarin and Sulfocoumarin Dyes

	λ_{max}	E^{red}	No. of Steps
	467	– 1.40	10.8
	420	– 1.64	10.2
	435	– 1.30	11.0
	449	– 1.40	12.5
	460	– 1.42	12.5
	415	– 1.44	9.0

Oxanol Dyes

		λ_{max}	E^{red}	No. of Steps
	*n* = 2	656	– 0.95	10.2
	n = 1	553	– 1.20	11.5
	n = 0	453	– 1.48	10.0

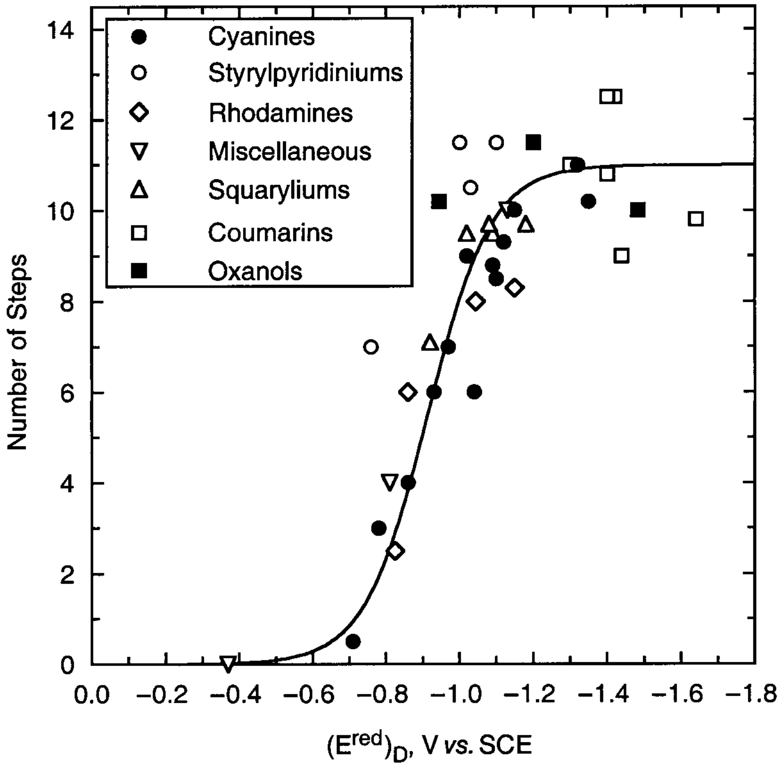


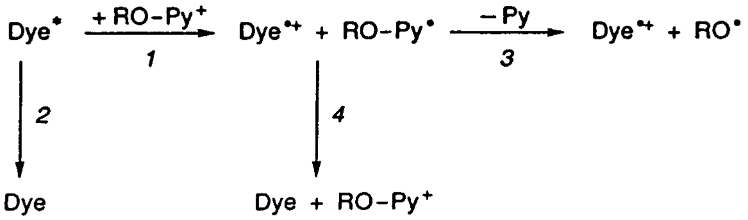
Figure. *Plot of the efficiency of photoinduced polymerization* vs. *the reduction potential of sensitizing dyes from different classes, with the* N*-alkoxypyridinium* **A1** *as the radical generator.* The polymerization efficiency is measured as the number of steps remaining after exposure through a neutral density step-tablet filter (see text for details).

Although there is considerable scatter in the data, there is a clear increase in efficiency of polymerization as the dye reduction potential becomes more negative, with essentially no initiation for dyes with reduction potentials less negative than *ca.* -0.7. This is exactly the behavior expected from the discussion of the energetics of the primary photoinduced electron transfer above. For dyes with reduction potentials more negative than -0.7 eV, the initiation efficiencies rapidly increase with increasingly negative reduction potential, and then levels off at values more negative than -1.1 V *vs.* SCE, when the electron-transfer process becomes exothermic.

The *Figure* clearly indicates that, for the dyes studied, the reduction potential is the main factor that controls the polymerization-initiation efficiency. The scatter, however, is certainly a consequence of the fact that other factors play a role. The overall efficiency of initiation is related to the corresponding efficiency for generation of free radicals, which is determined by two sets of competitive processes, as shown in *Scheme 3*.

The reaction of the excited dye (Dye*) with the alkoxypyridinium ($RO-Py^+$) (*Scheme 3*, *Path 1*) competes with the deactivation reactions of the excited dye

Scheme 3



(*Path 2*). The rate of the reaction in *Path 1* is determined by the concentration of the alkoxypyridinium and the rate constant for the electron-transfer reaction. The rate of the second reaction (*Path 2*) is determined by the sum of all radiative and nonradiative decay paths of the excited dye, and can vary over a wide range [21]. The next competing processes are the fragmentation of the pyridyl radical ($RO-Py^{\bullet}$) to give the alkoxy radical ($RO^{\bullet}$) (*Path 3*), and return electron transfer (*Path 4*), which is an energy-wasting step that regenerates the starting materials. Although the fragmentation reaction does not depend on the dye, the return electron-transfer reaction certainly varies with the chemical nature and the oxidation potential of the dye [22], and thus may also occur with a wide range of rates [22].

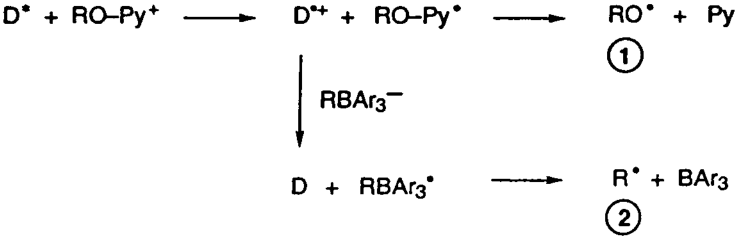
In addition to these variables, because a broad-spectrum light source was used for irradiation, the amount of light absorbed by the different dyes varies as a function of the width of the absorption bands. The spectral distribution of the Xe-lamp output is also uneven across the visible region. All of these factors should contribute to scatter in the data, especially between the different classes of dyes. In spite of all this, it is remarkable that a clear dependence on a single parameter, the reduction potential of the dye, is still quite evident.

The deviation or scatter in the data is more pronounced with the coumarin and with the styrylpyridinium dyes. The highest efficiency observed with two sulfocoumarins may be due to additional reaction from the triplet state [23]. The low efficiency of the coumarins with the highest reduction potential (see *Table 1* and the *Figure*) is largely because these compounds have also the shortest-wavelength absorption, with a significant portion of the band being in the UV, which was filtered off. The relatively high efficiency of the styrylpyridiniums may be partly due to broader absorption bands, hence more-efficient light capture.

The dyes that have the highest practical value are obviously those that exhibit high initiation efficiency, have appropriate physical properties, such as compatibility with the polymerizable composition, and have good thermal stability [6]. The reduction potential, absorption maxima, and polymerization efficiency for all of the dyes studied here are summarized in *Table 1.* The thermal stability of these dyes in the polymerization composition were determined by comparing the initiation efficiency of freshly prepared coatings with those after keeping at room temperature in the dark for several months. Nearly all the dyes listed in *Table 1* were found to meet this requirement. Several samples were tested after storage for periods as long as two years and showed no significant change in performance.

2.6. *Double Fragmentation.* In addition to the formation of a radical in the sensitized cleavage of an alkoxypyridinium salt, a radical cation, namely that of the oxidized donor ($D^{\bullet +}$), is also formed. It occurred to us that it would be interesting to try to utilize the chemical energy stored in this radical cation to further enhance the desired photopolymerization process. As mentioned above, oxidative cleavage of alkyltriarylborates ($RBAr_3^-$) yields an alkyl radical [5]. The radical cation of the dye ($D^{\bullet +}$) formed in the sensitized reductive cleavage of an alkoxypyridinium ($RO-Py^+$) could in principle participate in a second electron transfer reaction with an alkyltriarylborate to generate a second radical. In this way, *two* initiating radicals could be produced for each absorbed photon, $RO^\bullet$ and $R^\bullet$ (① and ②, resp., *Scheme 4*).

Scheme 4

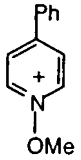
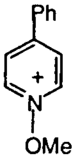
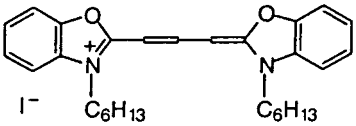
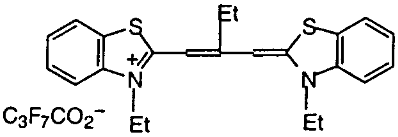


The feasibility of this concept was demonstrated by adding *both* the alkoxypyridinium **A1** and butyltriphenylborate to a polymerizable coating [24]. Sensitizing dyes were chosen as usual so that they had reduction potentials that were more negative than that of the alkoxypyridinium, to ensure that the electron transfer from the excited dye to the alkoxypyridinium was exothermic. One extra criterion was that the dyes were also chosen to have oxidation potentials that were more positive than that of the borate, to ensure that the electron-transfer reaction from the borate to the oxidized dye would also be exothermic. Thus, the dyes were capable of initiating polymerization either with the alkoxypyridinium or with the borate independently.

The results are shown in *Table 2*. The 1:1 combination clearly showed an approximate doubling in speed compared to those when either initiator was used alone. This result obviously provides strong support for *Scheme 4*.

3. Conclusions. – Practical and efficient sensitizing-dye systems that are useful for photoinitiation of polymerization reactions with *N*-methoxy-4-phenylpyridinium tetrafluoroborate salt are described. The fragmentation of the radical formed upon reduction of this compound is shown to be exothermic by *ca.* 138 kJ/mol, and thus should occur readily. It is further shown that the most important factor controlling the overall efficiency is the thermodynamics of the initial photoinduced electron-transfer reaction. A very simple relationship is described and tested that illustrates that the process is efficient when the reduction potential of the dye is equal to or more negative than that of the alkoxypyridinium, *i.e.*, *ca.* ≤ -1.0 V *vs.* SCE. Finally, from a combination of alkoxypyridinium and alkyltriarylborate salts with suitable sensitizers, two radicals can be generated per absorbed photon, thus doubling the overall polymerization efficiency.

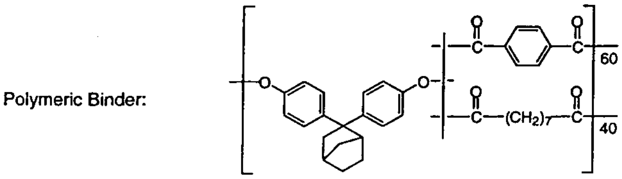
Table 2. *Relative Efficiencies of Photopolymerization with Cyanine Dyes as Sensitizers and Methoxypyridinium*[a]) *or Borate*[b]) *Activators or Both Activators*

Dye \ Activator(s)		$Bu{-}BPh_3^-$	 $Bu{-}BPh_3^-$
	(1.0)	~0.7	1.5–2.5
	(1.0)	~0.7	1.5–2.0

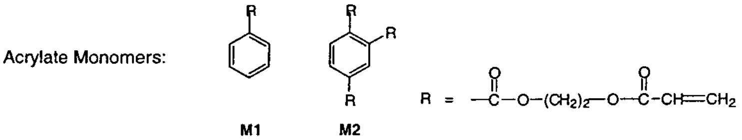
[a]) Counter ion: BF_4^-. [b]) Counter ion: NBu_4^-.

Experimental Part

The reduction potentials of the cyanine dyes were taken from the literature [20], and those of the other dyes were measured in CH_2Cl_2 or in MeCN at a Pt microelectrode by square-wave voltammetry. The efficiency of the different dyes to initiate photopolymerization in the presence of the *N*-alkoxypyridinium salt **A1** was tested with equal amounts of a polymeric binder (**B**) and a 1:1 monomer mixture (**M1** and **M2**) to which a small amount of an inhibitor (**I**) was added.

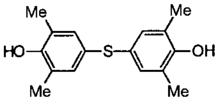


B



M1 **M2**

Inhibitor/Stabilizer:



I

To 10.3 g of CH_2Cl_2, 2.34 g of **B**, 1.17 g of **M1**, and 1.17 g of **M2**, and 12 mg of **I** were added. The **A1**, 77 mg (0.28 mmol) dissolved in 1 ml EtOH, was added to the polymerization mixture. The sensitizing dye, 0.02 mmol, was dissolved in the CH_2Cl_2 soln. or added to it as a conc. EtOH soln. The composition was hand coated on a copper sheet with a 0.3 mm coating knife and dried for 10 min at *ca.* 70°. A transparent polypropylene cover sheet was then placed over the coating. To ensure that the photopolymerization was induced by only excitation of the sensitizing dyes, cut-off filters (*W-2A*, *W-16*, or *W-25 Kodak-Wratten* filters that absorb $\geq$99.9% of light of λ shorter than 400, 510, or 580 nm, resp.) were used. The samples were exposed through a *Kodak Sensitometric Step Tablet No. 14* with optical densities varying by 0.15 unit increments. The samples were exposed for 3 min by means of a *Nu-arc FT32L* flip-top plate-maker equipped with a 4000 watt pulsed Xe lamp. The exposed samples were heated for 10 min at 70° and spray-developed for 2 min with 1,1,1-trichloroethane. The response, which is a measure of the sensitizer efficiency, was measured by the number of steps retained as a result of exposure.

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