acid, and 30 mL of concentrated nitric acid was added dropwise. After the whole mixture was kept at 120 °C for 2 days, the reaction mixture was poured onto 300 g of crushed ice and organic materials were extracted several times with ether. The combined extract was dried over sodium sulfate, and the ether was removed under reduced pressure. The residual liquid was added to a mixture of 5 mL of water and 10 mL of chloroform, and the whole mixture was stirred for 1 h at room temperature. The precipitate was collected and washed several times with chloroform giving 6 g of the hydrate of **1h** (mp 77 °C) as a white solid. The solid was dissolved in 100 mL of toluene, and an azeotropic mixture of toluene and water was removed by distillation. The residue was distilled under reduced pressure giving 4.6 g (20% yield) of **1h** as a yellow liquid: bp 90 °C (8 mm); IR (liquid) 1730 cm^{-1} ($\nu_{C=O}$). NMR in $CDCl_3$ $\delta(Me_4Si)$ 9.70 (s, 1 H), 8.87 (s, 1 H), and 8.63 (s, 1 H).

Anal. Calcd for $C_9F_6H_3NO_3$: C, 37.70; F, 39.70; H, 1.05. Found: C, 37.95; F, 39.44; H, 1.20.

***m,m'*-Dinitro-α,α,α-trifluoroacetophenone (1i).** An attempt to prepare this compound by the nitration of **1g** was unsuccessful. However, the nitration of 1-(*m*-nitrophenyl)-2,2,2-trifluoroethyl alcohol (**2g**) by essentially the same method as described above gave the hydrate of **1i** (mp 70 °C). Azeotropic removal of water from the hydrate gave **1i** in 20% yield as pale yellow crystals; mp 64 °C; IR (KBr) 1740 cm^{-1} ($\nu_{C=O}$); NMR in $CDCl_3$ $\delta(Me_4Si)$ 9.32 (s, 1 H) and 9.14 (s, 2 H).

Anal. Calcd for $C_8F_3N_2O_5$: C, 36.38; F, 21.58; H, 1.14. Found: C, 36.34; F, 21.88; H, 1.17.

1-Aryl-2,2,2-trifluoroethyl alcohols (2a–i). 1-Phenyl-2,2,2-trifluoroethyl alcohol (**2a**) was prepared by the reduction of **1a** with lithium aluminum hydride in 75% yield; bp 95 °C (22 mm).[36] Other alcohols, **2b–i**, were obtained by reducing the corresponding ketones with aluminum 2-propoxide in 2-propanol in 80–90% yields.

1-Propyl-1,4-dihydronicotinamide (PNAH). Syntheses of PNAH, PNAH-*4-d*, and PNAH-*4,4-d_2* have been described in a previous paper.[15] Mass and NMR spectral analyses revealed that the deuterium contents in PNAH-*4-d* and PNAH-*4,4-d_2* were 99.5 ± 0.5 and 90.0 ± 0.5% of the theoretical values, respectively.

Product Analyses. A mixture of a substrate (0.2 mmol) and PNAH (0.2 mmol) in 10 mL of acetonitrile was stirred under an atmosphere of argon in the dark at 50 °C for 1 week in the presence (0.2 mmol) or absence of magnesium perchlorate. Water was added to the mixture, and the solvent was evaporated under reduced pressure. The residue was poured into water and organic materials were extracted with ether. The ether layer was dried over sodium sulfate, and the ether was removed under reduced pressure. Amounts of the substrate remained unreacted and the alcohols produced were quantitatively measured on VPC (Silicon DC-200, 1 m). No other products except for PNA^+ were detected on VPC, TLC (hexane–ethyl acetate 3/1), and NMR. Spectral data of the product alcohols agreed with those of the corresponding authentic samples.

Isotopic Ratio in the Product. Deuterium content in a product alcohol obtained by the reduction with PNAH-*4-d* was analyzed by mass spectrometry on a Simazu LKB-9000 GC-MS spectrometer (SE-52, 1 m). The spectrometer was equipped with a PACK 3000G-b Computing System to calculate the areas of appropriate peaks. At least two different samples were subjected to the spectroscopy, and scans were repeated at least eight times for a sample.

Kinetic Procedure. Acetonitrile was flushed with dry argon prior to use. Solutions for kinetic studies were prepared under an atmosphere of argon and placed in a UV cell (1 cm) equipped with a silicon rubber stopper. The cell compartment of the spectrometer was also filled with dry argon and kept at 50 ± 0.05 °C. As a standard procedure, both sample and reference cells were filled with solutions of a substrate (and magnesium perchlorate, when necessary) in acetonitrile to obtain a difference spectrum. Then, an acetonitrile solution of PNAH was injected into the sample cell by using a syringe to start the reaction. Otherwise the kinetics could not be followed, because the absorption of a substrate was large enough to interfere the observation on the change in the intensity of an absorption (λ_{max} = 354 nm) from PNAH. It was confirmed that the order of incubation of the reagents did not affect the kinetics. The kinetics was followed by observing the decrease in the intensity at 354 nm. However, in runs with high concentrations of a substrate ([S] > 1 × 10^{-2} M), longer wavelengths were employed for the monitoring (375 nm for **1a–1f**; 384 nm for **1g** and **1h**).

Nevertheless, the change in the intensity of the kinetic solution of **1i** was too small to be followed accurately. Fortunately, the solution showed new absorption with maxima at 440, 464, and 570 nm. The increase in the intensities of new absorptions corresponded to the decrease in the intensity at 354 nm with an isosbestic point at 388 nm.[25] The kinetics for **1i**, therefore, was followed by observing the increase in the intensities at 440 and 464 nm.

All runs gave good first-order plots over 3 half-lives with correlation coefficient better than 0.9995.

Acknowledgment. A.O. thanks the Ministry of Education, Japan, for support of this work.

Supplementary Material Available: Table V, a listing of boiling or melting points and NMR spectral data of the alcohols (1 page). Ordering information is given on any current masthead page.

Reduction by a Model of NAD(P)H. 30. Proof for the Electron–Proton–Electron-Transfer Mechanism

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Received March 10, 1980

Abstract: Kinetics for the reduction of the *N*-methylacridinium ion by 1-aryl-1,4-dihydronicotinamides in acetonitrile have been studied. The second-order rate constants are linearly correlated with the σ values of substituents. A Hammett-type plot for the kinetic isotope effect affords a Λ-shape correlation with the para methyl substituent as a maximum (k^H/k^D = 5.72), whereas the isotopic partitioning ratio in the product remains constant. The results have been interpreted in terms of an electron–proton–electron-transfer mechanism.

After extensive discussion of the mechanism of reduction with 1,4-dihydropyridine derivatives, it has been proposed that the reduction, in some cases, is most likely composed of initial electron transfer followed by transfer of a hydrogen nucleus.[1-11] In contrast to the initial transfer of an electron, the mechanism of the subsequent process has not yet been well understood. For the re-

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Table I. Rate Constants for the Reduction of the *N*-Methylacrydinium Ion (1) with 1-(4-Methoxyphenyl)-1,4-dihydronicotinamide (ANAH-a) in Acetonitrile at 50 °C[a]

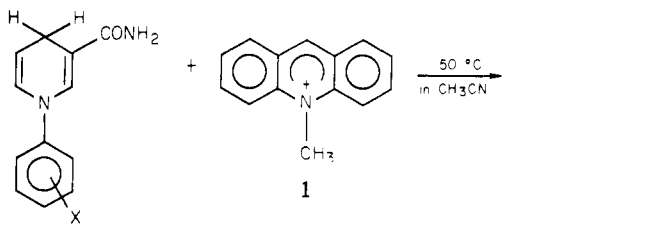
10^4[ANAH-a], M	$10^2 k_{obsd}$, s^{-1}	k_2, M^{-1} s^{-1}
2.30	0.849	36.9
2.43	0.910	37.4
3.17	1.15	36.3
4.11	1.53	37.2
4.59	1.70	37.0
7.94	2.96	37.3
		37.0[c] ± 0.362[b]

[a] [1] = 2.00×10^{-5} M. Errors in k_{obsd} were estimated to be <±3%. [b] Standard deviation. [c] Mean value.

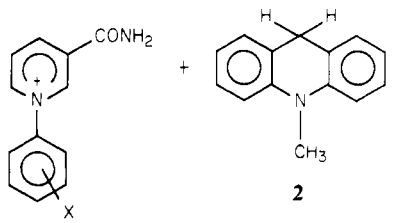
duction of thiobenzophenone, we proposed, based on an ESR study and product analyses, that the hydrogen nucleus undergoing the reaction was not accompanied by an electron. That is, the reduction proceeds through a three-step electron–proton–electron-transfer process.[5] The proposed mechanism, however, cannot be extended to the reduction of other substrates until further evidence is accumulated from a variety of reductions. Since the transfer of a hydrogen nucleus is more or less involved in the rate-determining step of the reduction, it is not easy to ascertain whether the moving hydrogen nucleus is accompanied by an electron (hydrogen atom transfer) or not (proton transfer). To obtain further insight into the mechanism, we studied the reduction of *N*-methylacridinium ions (*1*) by various 1-aryl-1,4-dihydronicotinamides (ANAH's). The reduction of **1** with an dihydropyridine derivative has been studied by several groups.[6b,12,13]

Results

Kinetics for the reduction of **1** with substituted and unsubstituted ANAH's was studied in acetonitrile at 50 ± 0.05°C.



ANAH-a-h



ANA⁺-a-h

a, X = *p*-CH_3O; b, X = *p*-$PhCH_2O$; c, X = *p*-CH_3; d, X = H; e, X = *p*-Br; f, X = *m*-Br; g, X = *m*-CF_3; h, X = *p*-CN

The reduction was first order in **1** and first order in ANAH. The observed rate constants, k_{obsd}, at appropriate concentrations of ANAH-a are listed in Table I together with the calculated second-order rate constants, k_2. Practically no autodecomposition of ANAH-a was detected. The second-order rate constants for other ANAH's and their 4-deuterio analogues, ANAH-*4-d*, are summarized in Table II.

Table II. Second-Order Rate Constants for the Reduction of the *N*-Methylacridinium Ion (1) with 1-Aryl-1,4-dihydronicotinamides (ANAH) and Their 4-Deuterio Analogues (ANAH-*4-d*) in Acetonitrile at 50 °C[a]

X in ANAH	k_2, M^{-1} s^{-1} with ANAH	k_2, M^{-1} s^{-1} with ANAH-*4-d*
p-CH_3O	37.0 ± 0.362	22.4 ± 0.173
p-$PhCH_2O$	35.1 ± 0.665	21.2 ± 0.393
p-CH_3	25.2 ± 0.206	14.8 ± 0.111
H	14.0 ± 0.232	8.55 ± 0.0541
p-Br	5.31 ± 0.0647	3.27 ± 0.0462
m-Br	3.35 ± 0.0697	2.16 ± 0.0167
m-CF_3	2.41 ± 0.0120	1.57 ± 0.0429
p-CN	0.945 ± 0.00768	0.683 ± 0.00409

[a] Errors are standard deviations.

Table III. Deuterium Kinetic Isotope Effect (k^H/k^D) and Isotopic Distribution in the Product (Y^H/Y^D) in the Reduction of the *N*-Methylacridinium Ion (**1**) with 1-Aryl-1,4-dihydronicotinamide (ANAH) in Acetonitrile at 50 °C[a]

X in ANAH	k^H/k^D	Y^H/Y^D
p-CH_3O	4.74	5.9
p-$PhCH_2O$	4.81	
p-CH_3	5.72	5.9
H	4.51	5.7
p-Br	4.31	6.1
m-Br	3.45	5.9
m-CF_3	3.30	6.2
p-CN	2.25	
		6.0[c] ± 0.16[b]

[a] Estimated errors are ±4% for k^H/k^D and ±7% for Y^H/Y^D. [b] Standard deviation. [c] Mean value.

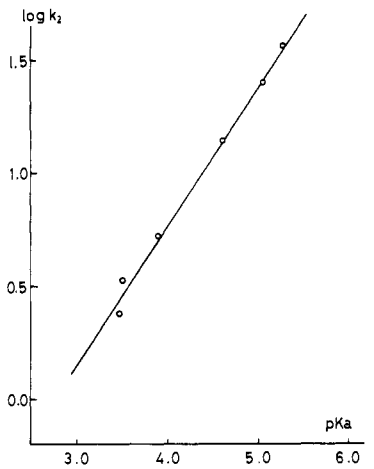


Figure 1. A plot of the logarithm of the second-order rate constant for the reduction of the *N*-methylacridinium ion with 1-aryl-1,4-dihydronicotinamide against the pK_a of the corresponding arylamine.

Product analyses revealed that *N*-methylacridan (**2**) and 1-aryl-3-carbamoylpyridinium (ANA^+) were the sole products and that the reduction proceeded quantitatively.

Discussion

A plot of logarithms of the second-order rate constants against σ values of the substituents gives a good linear relationship with $\rho = -1.75$ (correlation coefficient $r = 0.996$). In Figure 1 the logarithms of the second-order rate constants are also plotted against pK_a's of the corresponding substituted anilines.[14] The Brønsted-type linear relationship shown in Figure 1 (slope = 0.612, $r = 0.996$) indicates that the reactivity of an ANAH is largely

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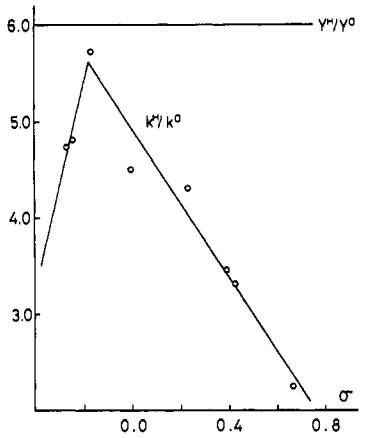


Figure 2. A plot of the kinetic isotope effect, k^H/k^D, against σ of the substituent for the reduction of the *N*-methylacridinium ion with 1-aryl-1,4-dihydronicotinamide.

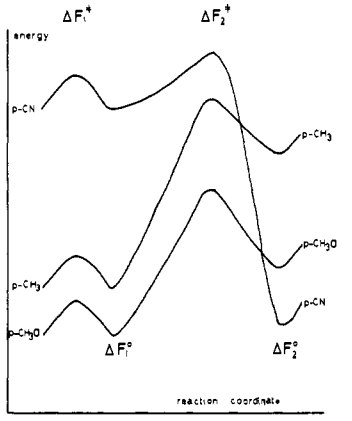
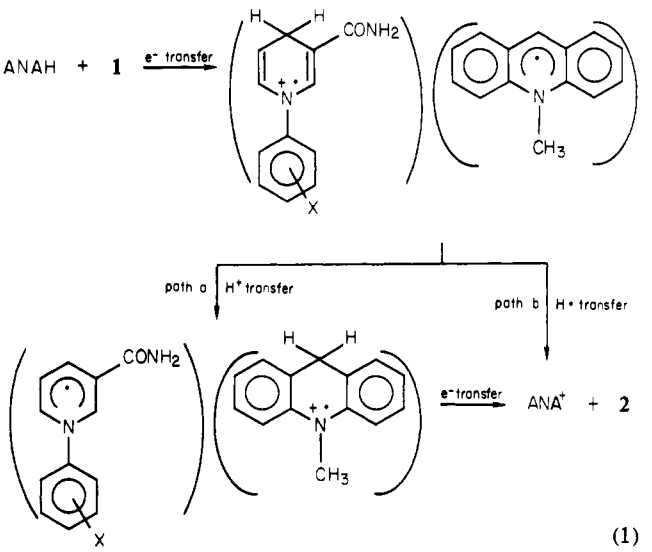


Figure 3. Schematic illustration for the energy diagram of the reduction by representative ANAH's.

affected by the lone-pair electron density on the ring nitrogen. The result is in agreement with our previous proposal that the driving force of the reduction originates from the removal of an electron or electron pair on the ring nitrogen.[9,11,15]

Kinetic isotope effects, k^H/k^D, calculated from Steffens and Chipman's equation[8] and isotopic partitioning ratios in **2** (product isotope effect), Y^H/Y^D, are listed in Table III.[16] In contrast to the linear relationship between log k_2 and σ, a plot of k^H/k^D against σ affords a bent line with ANAH-c as the maximum point as shown in Figure 2. The variation of k^H/k^D cannot be accounted for by the change in the position of the transferring hydrogen nucleus at the transition state of the reduction, because Y^H/Y^D's remain constant for all ANAH's. The existence of discrepancies between the values of corresponding k^H/k^D and Y^H/Y^D suggests that the movement of a hydrogen nucleus is only partly involved in the transition state of the reduction.[17] However, there is no doubt, based on the large kinetic and product isotope effects, that the process involving the movement of a hydrogen nucleus is the major rate-determining step of the reduction. In other words, the above results suggest that there exists a preequilibrium before a hydrogen nucleus is transferred and the equilibrium constant is susceptible to the substituent effect. The constancy of Y^H/Y^D again indicates that the isotope effect for the preequilibrium is very small, if any.[6b] It has been reported that **1** and 1-benzyl- or 1-propyl-1,4-dihydronicotinamide (BNAH or PNAH) form a charge-transfer complex,[6b,13] and we reported that the initial transfer of an electron is a universal phenomenon for the reduction with a 1,4-dihydropyridine derivative.[11] Although we could not obtain unequivocal evidence for the presence of a charge-transfer intermediate in the present reduction system, there remains no doubt that the reduction proceeds through an initial one-electron transfer, on the basis of the above discussion.

For interpretation of the substituent effects shown in Figures 1 and 2, an energy diagram schematically illustrated in Figure 3 is helpful. In Figure 3, relative energy levels for the transition state of the initial one-electron-transfer (ΔF_1^*), the charge-transfer intermediate (ΔF_1°), the transition state for the transfer of hydrogen nucleus (ΔF_2^*), and the products (ANA^+ and **2**) or the



(1)

second intermediate (a pair of ANA· and 2^{+}·) (ΔF_2°) are shown. The stabilities of the radical cations of ANAH's can reasonably be expected to decrease with the increase of electron-withdrawing ability of the substituent. The expectation is supported by the fact that the half-peak oxidation potentials[18] and dimerization rates[19] of aryldiphenylamines are linearly correlated with the σ^+ values of the substituents. Consequently, ΔF_1°'s (and hence ΔF_1^*'s, too) are arranged in such a way that an electron-withdrawing substituent increases the energy level of the intermediate.

The Hammett relationship observed for the second-order rate constants undoubtedly suggests that an electron-withdrawing substituent also elevates the level of ΔF_2^*'s. However, in order to account for the relative magnitudes of kinetic isotope effects, we should arrange the value of $\delta\Delta F^* = \Delta F_2^* - \Delta F_1^*$ or $\delta\Delta F = \Delta F_2^* - \Delta F_1^\circ$ should be arranged in the order: *p*-CH_3O < *p*-$PhCH_2O$ < *p*-CH_3 > H > *p*-Br > *m*-Br > *m*-CF_3 > *p*-CN.

We are now in the position to discuss whether the charge-transfer intermediate undergoes the reaction through path a or path b shown in eq 1. If path b is involved, the process would afford a nitrogen cation (ANA^+) from a nitrogen radical cation ($ANAH^+$·). Since the substituent effect for the stability of an aromatic nitronium ion is of the same order of magnitude as the effect for the corresponding radical cation (cf. Figure 1), there exists no factor to increase the transition energy for the hydrogen atom transfer from (ANAH-c^+·) to the maximum regardless of whether the transition state is reactant-like or product-like. On the other hand, if the reaction proceeds via path a, one of the products would be a free radical (ANA·). The stability of a free radical is defined by spin density on the central atom, and the spin density is related to the hyperfine splitting constant, a, in the ESR spectrum of the radical. It has been reported that both electron-releasing and -withdrawing substituents reduce a for *N-tert*-butylanilino radicals.[20] A similar trend can be seen in a

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Table IV. Second-Order Rate Constants and Kinetic Parameters for the Reductions with 1-Aryl-1,4-dihydronicotinamides (ANAH-c and ANAH-h)

temp, °C	k_2, M^{-1} s^{-1}	
	ANAH-c	ANAH-h
25		0.203 ± 0.0123
30	10.7 ± 0.229	0.281 ± 0.00500
35		0.373 ± 0.00830
40	16.2 ± 0.295	0.536 ± 0.0116
50	25.2 ± 0.206	0.945 ± 0.00768
60	34.8 ± 0.520	
$\Delta H^{\ddagger}$, kcal/mol[a]	7.37	11.2
$\Delta S^{\ddagger}$, cal/(mol deg)[a]	−29.7	−24.2
$\Delta F^{\ddagger}$, kcal/mol[a]	17.6	19.0

[a] Values at 50 °C.

series of para-substituted cumyl radicals.[21] Thus, the variation of kinetic isotope effect can be attributed to the substituent effect on radical species produced by a proton transfer from $ANAH^{+\cdot}$.

Table IV lists kinetic parameters and second-order rate constants at various temperatures for the reductions with ANAH-c and ANAH-h, two ANAH's which have exerted maximum and minimum kinetic isotope effect, respectively. The kinetic parameters indicate that the reduction with ANAH-h is less dependent upon the entropy term than the reduction with ANAH-c. This observation supports the idea described above; the transition state of the reduction with ANAH-c is largely dominated by the proton-transfer process, whereas that with ANAH-h is mainly constituted of the initial electron-transfer process. Consequently, the transition state of the former reduction is tighter than that of the latter reduction.

Van Eikeren and Grier reported the value of Y^H/Y^D to be 6.2 for the reduction of BNA^+ with BNAH in acetonitrile.[10] The value is identical with the present result within experimental error, which indicates that the present reduction involves a symmetric transition state with respect to the migrating hydrogen nucleus. The proton-transfer mechanism also agrees with symmetry considerations: both sides of the transition state are composed of a radical cation and a free radical of similar structures.

We believe that the proton-transfer mechanism is universal for the reduction with a 1,4-dihydropyridine derivative, because a proton is transferred to a neutral species in the present reduction. When a neutral molecule is employed as a substrate, the corresponding proton acceptor is a radical anion, which might have larger affinity for a proton ($Y^H/Y^D \simeq 4$)[11] than a neutral radical ($Y^H/Y^D \simeq 6$). We would like to emphasize again, however, that the driving force for the proton-transfer process is the proton-releasing power of $ANAH^{\cdot+}$ instead of the proton-seeking power of a substrate as described in the beginning paragraph of this discussion.

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In conclusion, we would like to propose that the reduction with a 1,4-dihydropyridine derivative proceeds through a three-step electron–proton–electron-transfer process and the facility of the initial transfer of an electron governs the rate of the reduction. Whether or not the transition state for the proton-transfer step has the maximum energy along the reaction coordinate depends on the properties of reagents.[7,11]

Experimental Section

Melting and boiling points were not corrected. UV, IR, and NMR spectra were recorded on a Union Giken SM-401, Hitachi EPI-S2, and JEOL JNM-FX 100 spectrometers, respectively.

Materials. Acetonitrile was distilled three times over phosphorous pentoxide and stored over 4A molecular sieves under an atmosphere of argon.

1-Aryl-3-carbamoylpyridinium perchlorates ($ANA^+ClO_4^-$) were prepared by exchange reactions of 1-(2,4-dinitrophenyl)-3-carbamoylpyridinium chloride[22] with the corresponding anilines,[23] followed by the treatment with sodium perchlorate. 1-Aryl-1,4-dihydronicotinamides (ANAH) and their 4-deuterio derivatives (ANAH-*4-d*) have been prepared by the procedure previously reported.[24] *N*-Methylacridinium iodide (**1**) was prepared according to a literature procedure.[25]

Product Analyses. A mixture of 2 mmol of *N*-methylacridinium iodide and 2 mmol of an ANAH in 10 mL of acetonitrile was reacted for 1–3 days at room temperature in the dark. The reaction was quenched by the addition of 10 mL of water. The yields of *N*-methylacridan (**2**) were quantitative (>99%) as measured on a Yanagimoto G-1800F vapor-phase chromatograph (5% Silicon DC-200, 1 m, 160 °C).

Isotopic Ratio in the Product. Deuterium content in the product, **2**, obtained by the reduction with ANAH-*4-d*, was analyzed by mass spectrometry on a Shimazu LKB-9000 GC-MS spectrometer (Silicon DC-200, 1 m).[11] The spectrometer was equipped with a PACK 3000G–b Computing System to calculate the areas of appropriate peaks. At least two different samples were subjected to the spectroscopy, and scans were repeated at least eight times for a sample.

Kinetics. Acetonitrile was flushed with dry argon prior to use. The solutions for kinetic studies were prepared under an atmosphere of argon and placed in a UV cell (1 cm) equipped with a silicon rubber stopper. The cell compartment of the spectrometer was also filled with dry argon and kept at 50 ± 0.05 °C. As a general procedure, the pseudo-first-order decrease of *N*-methylacridinium iodide was followed by observing the decrease in the intensity of absorption at 420 nm ($\epsilon \simeq 4800$). All runs gave good first-order plots over 3 half-lives with correlation coefficients better than 0.999.

Supplementary Material Available: Tables V and VI, lists of color, melting point, and IR ($\nu_{C=O}$) of $ANA^+ClO_4^-$ and ANAH, Table VII, a list of absorption maximum and NMR data for ANAH, Table VIII, a list of elemental analyses for ANAH (4 pages). Ordering information is given on any current masthead page.

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