

gen or degassed and were irradiated in a "merry-go-round" apparatus using a PEK No. 202 high-pressure Hg arc lamp with the light collection system. The collimated light was filtered through a water jacket (20-cm length) and either a Corning filter (CS 5-60) or a  $\text{NaNO}_2/\text{K}$  acid phthalate solution to provide a transparent window in the 405–436-nm region. The potassium ferric oxalate actinometry described by Hatchard and Parker<sup>26</sup> was adapted. The duration of irradiation was usually 2–3 hr during which the optical density of the monitoring peaks (405 and 425 nm) decreased by 15–25%.

Some quantum yields obtained by the above method were checked by a split beam irradiation apparatus similar to that described by Beckett and Porter.<sup>25</sup> The agreements of the results by two methods were within  $\pm 2\%$ .

**Flash Photolysis.** The preliminary experiment was carried out with a 5  $\mu\text{sec}$  dual beam flash kinetic apparatus using a pulsed monitoring light source as previously described. The subsequent kinetic studies utilized an improved apparatus with 0.8 and 0.5  $\mu\text{sec}$  flash durations. This consists of two independent, synchronously triggered capacitor-spark gap lamp circuits. The 0.8- $\mu\text{sec}$  apparatus used two 0.3- $\mu\text{F}$  25-kV capacitors (one in each circuit).<sup>33</sup> For the 0.5- $\mu\text{sec}$  apparatus, two 0.05- $\mu\text{F}$  35-kV capacitors were used.<sup>34</sup> The lamp configuration and the procedure were

(33) R. W. Yip, W. D. Riddell, and A. G. Szabo, *Can. J. Chem.*, **48**, 987 (1970).

(34) G. Porter, R. W. Yip, J. M. Dunstin, A. J. Cessna, and J. E. Sugamori, *Trans. Faraday Soc.*, **67**, 3149 (1971).

the same as that reported.<sup>35</sup> The decay curve of the transient was analyzed by plotting the logarithm of the optical density *vs.* time which gave a straight line. The data were processed by a computer program made available by Dr. A. G. Szabo, Division of Biology, National Research Council, Ottawa. The optical density of the transient 2  $\mu\text{sec}$  after the termination of photoflash is taken as the initial OD.

**Quenching of NMA. Decomposition by Stilbenes and Pterylenes.** Commercial *trans*-stilbene in benzene was irradiated in a Pyrex apparatus under nitrogen. A vpc analysis (Apiezon N column, 8 ft  $\times$   $\frac{1}{8}$  in.) showed that the retention times for *cis*- and *trans*-stilbene were 3.8 and 8.2 min and the ratio was 90.5:9.5.

Solutions containing NMA ( $4.7 \times 10^{-3}$  M) and *trans*-stilbene ( $4.07 \times 10^{-5}$  M to  $4.07 \times 10^{-3}$  M) were degassed and irradiated as described in the quantum yield determination. The nitrosamide absorptions at 403 and 426 nm decreased by 25% in 2.5 hr of irradiation.

The variation of the quantum yield was less than 10% when the concentration of *trans*-stilbene was less than  $10^{-3}$  M. The ratio of *cis*- to *trans*-stilbenes was shown to be 1.5:98.5 before the irradiation and 1:99 after the irradiation. When *cis*-stilbene was used for a similar quenching experiment, the result was the same; the ratio of *cis*- to *trans*-stilbenes was 90.2:9.8 before and after the irradiation, during which 30% of NNO had decomposed.

The ratio of *cis*- to *trans*-piperylene was analyzed by vpc on a 30%  $\text{AgNO}_3/\text{TEG}$  on 25% firebrick (5 ft  $\times$   $\frac{1}{8}$  in.) at 42°.

(35) R. W. Yip, *Rev. Sci. Instrum.*, **40**, 1035 (1969).

## Polar Effects of the Aminium Radical Addition to Styrenes<sup>1</sup>

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**Abstract:** In order to study the polar effects of the aminium radicals generated by the photolysis of nitrosamines, the relative reactivities of eight meta- and para-substituted styrenes toward the piperidinium radical addition were determined by the competitive method in methanol containing dilute hydrochloric acid. The electric requirements were shown to correlate better with  $\sigma$  constants giving the  $\rho$  value of  $-1.34$  but not with  $\sigma^+$  constants. Comparisons of the known  $\rho$  values for various radical addition reactions led us to conclude that the polar effects were caused by ground state electrostatic attraction between the positive charge of the aminium radical and the  $\pi$  electron of styrenes rather than resonance stabilization at the transition state. The quantum yield of the *N*-nitroso-piperidine photoaddition to styrene was dependent on the nitrosamine concentration but not on the styrene concentration indicating the presence of chain processes.

In the recent years, polar effects of radical reactions<sup>2</sup> have been a subject of intense investigations in a hope to delineate nonrandom reactivity of radicals. For a quantitative treatment of the polar effects, Hammett-type substituent effect-reactivity correlation has been widely utilized to unravel the radical reaction mechanism. Competitive hydrogen abstractions of various radicals from meta- and para-substituted toluenes have been widely used techniques to obtain Hammett correlations with considerable success.<sup>2</sup> However, there are only a few cases of the similar correlation on radical addition to meta- and para-substituted styrenes and the corresponding stilbenes in the literatures.<sup>3–5</sup> All of the radicals studied in these hydrogen

abstraction and addition reactions give negative reaction constants ( $\rho$  values) of various size and generally correlate better with  $\sigma^+$  constants than with  $\sigma$  constants.

We have established that photolysis of a *N*-nitrosodialkylamine in dilute acid solution generates nitric oxide and the aminium radical, the latter of which undergoes hydrogen abstraction or addition to a double bond.<sup>6</sup> Aminium radicals have been generated by a metal ion catalyzed decomposition<sup>7</sup> or photolysis<sup>8</sup> of *N*-chloramines under strongly acidic conditions (for example, 4 M  $\text{H}_2\text{SO}_4$  in AcOH). There exists good evidence that an aminium radical is an electrophilic species

(1) Photoreactions of Nitroso Compounds in Solution. XXVII. For part XXVI, see J. N. S. Tam, R. W. Yip, and Y. L. Chow, *J. Amer. Chem. Soc.*, **96**, 4543 (1974).

(2) For a general review of this subject, see the recent monograph by G. A. Russell in "Free Radicals," Vol. 1, J. Kochi, Ed., Wiley, New York, N. Y., 1973, p 275.

(3) H. Sakurai, S. Hayashi, and A. Hosomi, *Bull. Chem. Soc. Jap.*, **44**, 1945 (1971).

(4) J. I. G. Cadogan and I. H. Sadler, *J. Chem. Soc. B*, 1191 (1966).

(5) G. A. Russell and R. C. Williamson, Jr., *J. Amer. Chem. Soc.*, **86**, 2357 (1964).

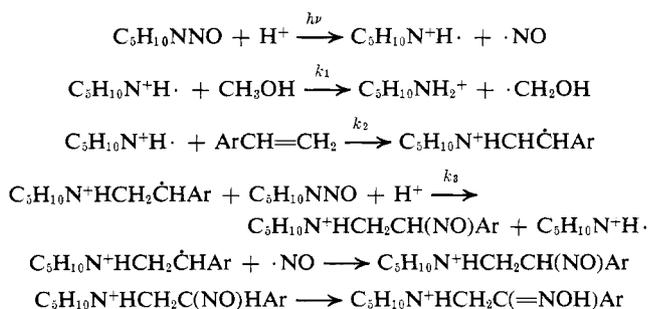
(6) M. P. Lau, A. J. Cessna, Y. L. Chow, and R. W. Yip, *J. Amer. Chem. Soc.*, **93**, 3808 (1971).

(7) F. Minisci, *Synthesis*, **1** (1973), and the previous papers quoted therein.

(8) R. S. Neale and E. Gross, *J. Amer. Chem. Soc.*, **89**, 6579 (1967), and the preceding papers from this research group.

due to the cationic charge carried by the radical.<sup>7-9</sup> However, the polar nature of such cationic radicals remains to be delineated quantitatively. Neale and Gross<sup>8</sup> have studied the relative reactivities of substituted toluenes toward the hydrogen abstraction by piperidinium radical  $(\text{CH}_2)_5\text{NH}\cdot^+$  generated from *N*-chloropiperidine in 2 *M*  $\text{H}_2\text{SO}_4$  in AcOH and have concluded that the presence of the positive charge on the piperidinium radical did not lead, under the chosen conditions, to an unusually enhanced polar effect of the aromatic substituents in attaining the transition state for the hydrogen abstraction (*vide infra*). In a hope to elucidate the addition mechanism of aminium radicals to olefins under dilute acidic conditions<sup>9</sup> and compare them with the same aminium radical generated under strongly acidic conditions,<sup>7,8</sup> competitive addition reactivities of the piperidinium radical, generated from the corresponding nitrosamine photolysis, to meta- and para-substituted styrenes were determined.

Under steady state irradiation, *N*-nitrosopiperidine (NNP) photolysis in methanol in the presence of dilute hydrochloric acid and a styrene is believed to follow the mechanism as shown below.<sup>9-12</sup>



Since the rate constant of piperidinium radical hydrogen abstraction from methanol<sup>6</sup> ( $k_1 = 4.8 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ ) is estimated to be about  $10^4$  times slower than its addition to styrene<sup>13</sup> ( $k_2$ ), the former step is negligible in comparison to the latter. From our flash photolysis studies,<sup>6</sup> it has been shown that the decay rate constant of the piperidinium radical is proportional to the concentration of an olefin but independent of the concentration of NNP.<sup>6,14</sup> As it will be shown later, the addition step to styrene ( $k_2$ ) is the rate-determining step and is necessarily slower than the propagation step ( $k_3$ ). However, the chain length of the photoaddition has not been determined; the quantum yield of the NNP photoaddition to cyclooctene has been shown to be in the vicinity of four.<sup>15</sup> Since the reactivity of styrenes, in terms of their absolute rate constants, toward the piperidinium radical is estimated<sup>13</sup> to be  $10^7$ – $10^8 \text{ M}^{-1} \text{ sec}^{-1}$ , their differences of activation energy will be fairly small. The competitive addition of two styrenes is adapted to obtain the reactivity ratio  $k_X/k_H$

(9) Y. L. Chow, *Accounts Chem. Res.*, **6**, 354 (1973).

(10) Y. L. Chow, M. P. Lau, R. A. Perry, and J. N. S. Tam, *Can. J. Chem.*, **50**, 1044 (1972).

(11) Y. L. Chow, C. J. Colón, and S. C. Chen, *J. Org. Chem.*, **32**, 2109 (1967).

(12) Y. L. Chow and C. J. Colón, *Can. J. Chem.*, **45**, 2559 (1969).

(13) Flash photolysis of NNP in the presence of *trans*-1,3-pentadiene, showed that the aminium radical reacted with the diene with the bimolecular rate constant of  $k_2 = 6.25 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ . A. J. Cessna, unpublished results.

(14) M. P. Lau, Ph.D. Dissertation, Simon Fraser University, Burnaby, British Columbia, 1970.

(15) C. J. Colon, Ph.D. Dissertation, Simon Fraser University, Burnaby, British Columbia, 1971.

where  $k_X$  and  $k_H$  are the observed pseudo-first-order rate constants of the piperidinium radical addition to styrene (standard) and to X-substituted styrene, respectively. The ratio therefore measures the partition of the piperidinium radical reaction toward two styrenes and represents the ratio of two different activation free energies of the additions.

## Experimental Section

Unless specified otherwise, the following experimental conditions prevailed. Nmr spectra were recorded with a Varian A56/60 spectrometer in  $\text{CDCl}_3$  solution using TMS as the internal standard. Chemical shifts were expressed in  $\tau$  values. A Perkin-Elmer RMU-6E mass spectrometer was used to record mass spectra. The ir spectra were recorded with a Perkin-Elmer 457 spectrophotometer as a Nujol mull or a liquid film. A Cary 14 spectrophotometer was utilized to monitor the kinetic disappearance of *N*-nitrosopiperidine. The vpc analyses were performed on a Varian 1400 instrument using a 20% SE 30 on Chromosorb W column using bromobenzene as the internal standard. The least-squares statistical analyses were carried out with a programmable Monroe Calculator 1670.

**Materials.** Commercially available (Aldrich) styrene, NNP, and bromobenzene were freshly distilled under reduced pressure immediately before the experiments.

All substituted styrenes except *p*-methoxystyrene were prepared by  $\text{KHSO}_4$  dehydration of the properly substituted phenylmethylcarbinols. The latter carbinols were synthesized either by the  $\text{NaBH}_4$  reduction of the appropriate acetophenones or by methylmagnesium bromide addition to the benzaldehydes. *p*-Methoxycinnamic acid was synthesized as described by Johnson<sup>16</sup> and was decarboxylated according to the known procedure<sup>17</sup> to give *p*-methoxystyrene, bp 92–93° (13 mm).

*p*-Cyanoacetophenone was prepared in 71% yield from *p*-bromoacetophenone and cuprous cyanide as reported by Friedman and Schechter.<sup>18</sup> Dehydration of the corresponding carbinol followed a modified method of Marvel and Overberger<sup>19</sup> and gave *p*-cyanostyrene as a yellowish liquid, bp 95–96° (20 mm). While a rigorously purified sample was stable under the conditions of the photoaddition, impure samples rapidly gave a cloudy solution in ethanol or methanol.

*m*-Acetamidostyrene was prepared by reductive acetylation of *m*-nitrostyrene based on the procedure of Landesberg, *et al.*,<sup>20</sup> and had mp 72–73° (reported mp 74–75°).

Other styrenes were prepared by standard procedures and exhibited the following boiling points: *p*-chlorostyrene (49° (32 mm)), *p*-methylstyrene (56–58° (12 mm)), *m*-bromostyrene (79–81° (20 mm)), *m*-methoxystyrene (79–80° (15 mm)), *m*-methylstyrene (53–56° (10 mm)).

All the substituted styrenes were purified before their use and exhibited the expected ir absorptions and nmr signals of the aromatic and olefinic (ABX multiplets) protons.

**General Conditions for Preparative Photoaddition.** In a photocell immersed in an ice bath a solution of a substituted styrene (0.01 mol), NNP (0.01 mol), concentrated hydrochloric acid (0.84 ml), and methanol (250 ml) was purged with nitrogen and irradiated with a medium pressure Hanovia Hg arc lamp (200 W) through a Norex filter for 1–1.5 hr. The progress of the photolysis was followed by the decrements of the 350-nm absorption band of NNP.

The photolysate was worked up in the usual manner as described before to afford the crude photoadducts.<sup>11,12</sup> The nmr spectrum of the crude products showed two singlets for the  $\beta$ -methylene protons corresponding to syn and anti oximes; the integration was used to calculate the ratio.<sup>12,21</sup> The predominant syn oxime was obtained by fractional recrystallization from methanol; generally the anti isomer was not isolated in pure state. The physical data and analysis of these oximes are listed in Table I.

**Kinetic Studies of Competitive Photoaddition of *N*-Nitrosopiperidine.** In all the kinetic studies, a stock solution (25 ml) containing

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(17) L. J. Kitchen and C. B. Pollard, *J. Amer. Chem. Soc.*, **69**, 854 (1947).

(18) L. Friedman and H. Schechter, *J. Org. Chem.*, **26**, 2522 (1961).

(19) C. S. Marvel and C. G. Overberger, *J. Amer. Chem. Soc.*, **67**, 2251 (1945).

(20) J. M. Landesberg, L. Katz, and C. Olsen, *J. Org. Chem.*, **37**, 930 (1972).

(21) Y. L. Chow and C. J. Colon, *J. Org. Chem.*, **33**, 2598 (1968).

**Table I.** The Yields and Physical Data of the Substituted  $\alpha$ -Piperidinoacetophenone Oximes

Substituent	Crude oximes				Syn oxime			
	Yield, % <sup>b</sup>	Ratio (syn:anti)	$\text{=CCH}_2\text{N}$ ( $\tau$ value) <sup>a</sup>	Ir, cm <sup>-1</sup>	Mp, °C	Analysis <sup>c</sup>		
						C	H	N
H	90	9:1	6.25 (1.8) 6.65 (0.2)	3150 979 940	117-117.5			
<i>p</i> -OCH <sub>3</sub>	80	9:1	6.25 (1.8) 6.70 (0.2)	3400 1075 835	108	67.97 (67.72)	8.25 8.12	11.38 11.28)
<i>p</i> -CH <sub>3</sub>	91 <sup>e</sup>	85:15	6.30 (1.7) 6.70 (0.3)	3400 995 825	144-145	72.68 (72.48)	8.75 8.68	12.18 12.06)
<i>p</i> -Cl	85	85:15	6.30 (1.7) 6.65 (0.3)	8160 1090 1070	137-138	61.89 (61.78)	6.84 6.78	11.29 11.08)
<i>p</i> -CN <sup>d</sup>	47	8:2	6.30 (1.6) 6.70 (0.4)	3250 2230 985 825	141-144			
<i>m</i> -Br	93	10:0	6.30	3310 1050	102-103	52.47 (52.54)	5.86 5.77	9.26 9.43)
<i>m</i> -OCH <sub>3</sub>	81 <sup>e</sup>	8:2	6.28 (1.6) 6.70 (0.4)	3280 1035	98-99	67.97 (67.72)	8.20 8.12	11.36 11.28)
<i>m</i> -CH <sub>3</sub>	81 <sup>e</sup>	10:0	6.28	3300 1035	92.5-93	72.33 (72.38)	8.72 8.68	11.94 12.06)
<i>m</i> -NHCOCH <sub>3</sub>	85	95:5	6.27 (1.85) 6.72 (0.15)	3310 985	157-158	65.49 (65.43)	7.61 7.69	15.40 15.26)

<sup>a</sup> The chemical shifts of the  $\alpha$ -methylene protons (singlet) in the mixture of the syn and anti oximes isolated from the photoaddition. The integration is given in parentheses. <sup>b</sup> The percentages are isolated yields of the mixture of the syn and anti oximes and represent the lower limit since thorough extraction gives additional 5-10% yields of the products. <sup>c</sup> The calculated per cents are given in parentheses below the corresponding "found" figures. <sup>d</sup> The sample was contaminated with a trace amount of bromide compounds. <sup>e</sup> Careful product analysis showed there were no other by-products such as those derived from hydrogen abstraction.

10<sup>-3</sup> mol each of styrene (standard substrate), a substituted styrene, NNP, and hydrochloric acid was prepared. Aliquots of 3.0 ml were pipetted into photolysis tubes fitted with a gas-purging device. Nitrogen was bubbled through each solution for 90-120 sec.

Five tubes containing the solution were placed in a merry-go-round apparatus immersed in a bath thermostated at 20° and were irradiated with a medium pressure Hanovia Hg arc lamp filtered with a Norex filter. The sixth tube protected from light with aluminium foil was kept in the water bath to serve as the control. At each 20-min interval, one tube was removed and at the fifth tube (100 min) generally 50-52% of NNP had reacted.

The irradiated solutions after being added with 0.5 ml of the bromobenzene solution (0.534 g in 10.0 ml of CH<sub>3</sub>OH) were used for vpc and uv analyses. The amount of NNP consumed in the irradiation was calculated from the decrease of the 350-nm absorption band. For each styrene, a calibration curve plotting the ratios of bromobenzene to the styrene *vs.* vpc integration readings was constructed. The amounts of an unreacted styrene were used to analyze the first-order rate constant of the disappearance of the styrene ( $k_H$  or  $k_X$ ) using a least-squares computation (Table II).

Competitive photoaddition to *p*-methoxystyrene and *p*-methylstyrene was carried out due to the fact that the latter reacted exclusively in the competition with styrene. The ratio of the rate constants was normalized by multiplying it by  $k_{p\text{-CH}_3}/k_H$  to give  $k_{p\text{-OCH}_3}/k_H$ . Even in competition against *m*-bromostyrene, no addition to *p*-cyanostyrene occurred; assuming that 5% of *p*-cyanostyrene had reacted during the photolysis,  $k_{p\text{-CN}}/k_H$  was estimated to be 0.085. The plot of the average of  $\log k_X/k_H$  against  $\sigma$  and  $\sigma^+$  values is shown in Figure 1.

**Quantum Yield Determination.** A potassium ferrioxalate actinometry solution as described by Hatchard and Parker<sup>22</sup> was placed in the photolysis tube and irradiated for 5 min under the same conditions as described above. This operation was repeated several times at each 15-min interval. The actinometry solutions were treated as described and the photon count was determined to be  $1.44 \pm 0.03 \times 10^{16}$  quanta/sec and reproducible.

In order to compensate for the unutilized photons due to the decrease in the nitrosamine 350-nm absorbancy as the photolysis pro-

**Table II.** The Competitive Photoaddition of NNP to Styrenes<sup>a</sup>

XC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> (0.04 M)	$k_X \times 10^5$ , sec <sup>-1</sup>	HC <sub>6</sub> H <sub>4</sub> - CH=CH <sub>2</sub> (0.04 M) <sup>d</sup>	$k_H \times 10^5$ , sec <sup>-1</sup>	$k_X/k_H$
<i>p</i> -CH <sub>3</sub>	10.39	H	5.70	1.82
	7.82		4.04	1.93
<i>p</i> -Cl	6.89	H	8.95	0.77
	4.45		6.72	0.66
<i>p</i> -OCH <sub>3</sub>	3.16		7.22	0.44
	3.21		5.70	0.57
<i>p</i> -OCH <sub>3</sub>	4.95	<i>p</i> -CH <sub>3</sub>	3.09	1.60
	6.82		4.18 <sup>b</sup>	1.63
<i>m</i> -CH <sub>3</sub>	4.10	H	3.21	1.28
	3.67		2.42 <sup>b</sup>	1.51
<i>m</i> -OCH <sub>3</sub>	6.55		4.94	1.32
	5.47	H	5.14	1.06
<i>m</i> -NHCOCH <sub>3</sub>	5.31		4.86 <sup>b</sup>	1.12
	4.09 <sup>b</sup>		3.67 <sup>b</sup>	1.09
<i>m</i> -Br	2.34	H	3.98	0.58
	1.39		2.72 <sup>b</sup>	0.52
<i>p</i> -CN	2.87	H	8.09	0.356
	2.57 <sup>b</sup>	<i>m</i> -Br	7.22	0.356
				(0.085) <sup>c</sup>

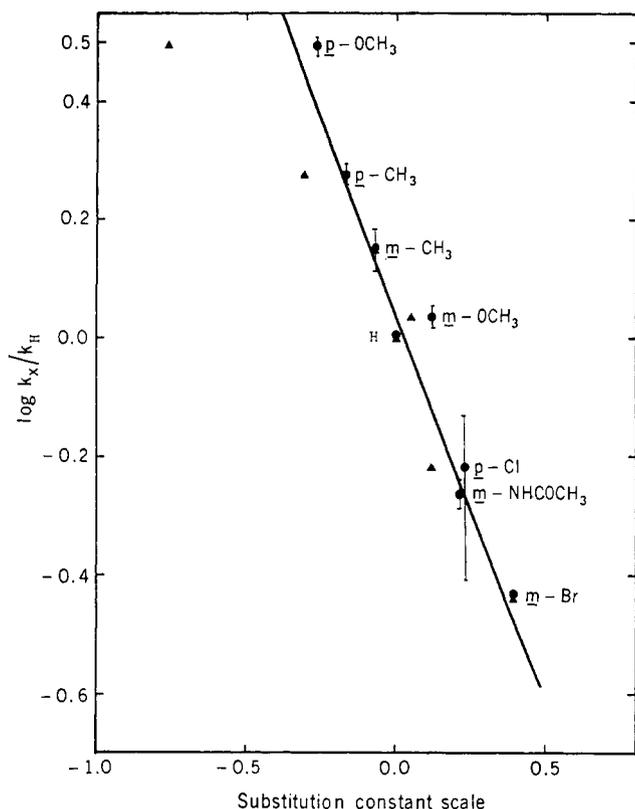
<sup>a</sup> Concentrations of NNP and hydrochloric acid were 0.04 M.

<sup>b</sup> Except for the calculations of these rate constants, the correlation coefficients ( $r$ ) from the computations are better than 0.985. <sup>c</sup> This ratio was estimated assuming 5% of *p*-cyanostyrene has reacted after 100 min. <sup>d</sup> The standard styrene used in the particular experiments.

ceeded, a calibration curve was constructed to provide *correction factors*. This was done by measuring the light filtering through solutions containing 0.040, 0.032, 0.024, 0.020, and 0.016 M NNP as well as in styrene with the ferrioxalate actinometry. The *correction factor* was defined as the ratio of the photon count striking at the actinometry solution from the unfiltered light to that from the filtered (through reacting solution) light.

Irradiation of a solution containing NNP, a styrene, and hydrochloric acid, all 0.04 M in concentration, in methanol was performed

(22) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, 235, 518 (1956).



**Figure 1.** The relative reactivities of substituted toluenes toward the piperidinium radical addition as a function of the substituent constants  $\sigma$  (●) and  $\sigma^+$  (▲). The points represent the average  $\log k_X/k_H$  and the vertical bars the ranges of experimental uncertainty.

**Table III.** The Photoaddition of NNP (0.04 M) to Styrenes (0.04 M)

$\text{XC}_6\text{H}_4\text{CH}=\text{CH}_2$	$k_X \times 10^4, \text{sec}^{-1}$	$\phi_N$
<i>p</i> -OCH <sub>3</sub>	0.77	6.18
<i>p</i> -CH <sub>3</sub>	0.72	7.08
<i>m</i> -CH <sub>3</sub>	1.13	7.50
H	1.36	7.95
<i>p</i> -Cl	0.69	10.14
<i>m</i> -Br	1.05	7.38
<i>p</i> -CN	0.64	10.14

**Table IV.** Variation of Concentrations in the Photoaddition of NNP to Styrene

[NNP], M	[Styrene], M	$k_H \times 10^4, \text{sec}^{-1}$	$\phi_N$
0.04	0.04	1.36	7.95
0.08	0.04	1.84	9.12
0.12	0.04	2.22	10.08
0.16	0.04	2.29	12.15
0.04	0.08	0.52	7.65
0.04	0.12	0.46	7.86

as described above. The quantum yields of NNP disappearance ( $\phi_N$ ) and the pseudo-first-order rate constant of the styrene reaction ( $k_H$ ) were calculated (Table III).

Keeping the concentration of styrene at 0.04 M, the concentrations of hydrochloric acid and NNP were varied successively by fourfold. The quantum yield  $\phi_N$  and the pseudo-first-order rate constant  $k_H$  were determined (Table IV).

In all the  $k_H$  plots, straight lines could be drawn with the points obtained up to 100 min of irradiation with correlation coefficients of better than 0.99. Similar types of  $\phi_N$  and  $k_H$  determinations by varying the concentration of styrene from 0.04 to 0.12 M were also

performed. Good straight-line correlations were obtained except for the  $k_H$  determination with 0.12 M styrene where relatively small decreases of styrene with respect to the high concentration of styrene made the vpc determinations less accurate. The data are summarized in Table IV.

## Results

In a methanolic solution containing dilute hydrochloric acid, NNP photolytically adds to styrene to give an excellent yield of *syn*- and *anti*- $\alpha$ -piperidinoacetophenone oximes. For the present kinetic investigation, the chosen substituted styrenes were stable under the adopted photolysis conditions and possessed no absorption above 300 nm. The initial concentrations of hydrochloric acid, NNP, and styrenes were fixed at 0.04 M each in methanol unless specified otherwise. Preparative scale photoaddition of NNP to these styrenes gave the expected acetophenone oximes (Table I); the total per cent of *syn* and *anti* oximes in each photoaddition indicated these styrenes reacted with the piperidinium radical very efficiently except for *p*-cyano-styrene. The drastically reduced reactivity of this styrene was demonstrated by the lower yield of the corresponding oximes and the isolation of *N*-piperidinoformamide, a photoreduction product, in methanol solution.<sup>6,10</sup>

The quantum yields of NNP disappearance ( $\phi_N$ ) and the pseudo-first-order rate constants of the styrene disappearance ( $k_H$  or  $k_X$ ) were determined under the identical conditions used in the kinetic studies except that only one styrene was present in the photolysis solution. As shown in Table III,  $\phi_N$  varied between 6 and 10 and irregularly with respect to the nature of substituent groups. Since the product analysis showed that the yields of the oximes were nearly quantitative, the  $\phi_N$  probably accurately represented the chain length of the addition reaction except the case of the addition to *p*-cyano-styrene. In the photoaddition to less reactive *p*-cyano-styrene, the piperidinium radical also underwent the reaction with methanol extensively and  $\phi_N$  represented the sum of the quantum yields of the addition and reduction processes.<sup>10</sup> Under the identical irradiation conditions, the observed rate constants  $k_X$  varied without a general trend since they were the product of two variables, namely the bimolecular rate constant  $k_2$  and the steady state concentration of the piperidinium radical. It was therefore necessary to use the competitive addition to obtain the relative reactivities.

The excellent straight plots for the  $k_H$  and  $\phi_N$  values regardless of the variations in NNP and styrene concentrations indicate that up to 100 min of reaction time the reaction pattern was not affected by the length of photolysis and the concentrations of the reactants. From Table IV it could be seen  $\phi_N$  remained constant as long as the NNP concentration was kept constant but increased when the concentration was raised. The latter was interpreted as an indication of increased chain length in the propagation step which also increased the steady state concentration of the piperidinium radical. This, in turn, increased the size of the observed rate constant for styrene addition since  $k_H = k_2[\text{C}_5\text{H}_{10}\text{NH}\cdot^+]$ . In the presence of a higher concentration of styrene, the lowering of  $k_H$  (Table IV) was to be expected since the steady state concentration  $[\text{C}_5\text{H}_{10}\text{NH}\cdot^+]$  was reduced. These measurements ascertained that the analytical procedures were satisfactory

Table V. The  $\rho$  Values of Some Radical Addition Reactions

Reactions	Temp, deg	Solvent	$\rho$	Ref
(1) $\text{HO}_2\text{CCH}_2\text{S}\cdot + \text{ArCH}=\text{CHPh}$	105	$\text{HSCH}_2\text{CO}_2\text{H}$	-0.4	4
(2) $\text{CH}_3\text{O}_2\text{CCH}_2\text{S}\cdot + \text{ArC}(\text{CH}_3)=\text{CH}_2$	105	$\text{HSCH}_2\text{CO}_2\text{CH}_3$	-0.52 <sup>a,c</sup>	
(3) $\cdot\text{CCl}_3 + \text{ArCH}=\text{CH}_2\text{Ph}$	105	$\text{CBrCl}_3$	-0.7	4
(4) $\cdot\text{CCl}_3 + \text{Ar}(\text{CH}_3)=\text{CH}_2$	105	$\text{CBrCl}_3$	-0.7 <sup>a</sup>	
(5) $\cdot\text{CCl}_3 + \text{ArCH}=\text{CH}_2$	80	$\text{C}_6\text{H}_6$	-0.42	3
(6) $\text{RO}_2\cdot + \text{ArCH}=\text{CH}_2$	60	$\text{C}_6\text{H}_6$	-0.3-0.4	5
(7) $\text{C}_5\text{H}_{10}\text{NH}\cdot^+ + \text{ArCH}=\text{CH}_2$	20	MeOH	-1.34 <sup>c</sup>	This work
(8) $\text{C}_5\text{H}_{10}\text{NH}\cdot^+ + \text{ArCH}_3$	20	2 M $\text{H}_2\text{SO}_4$ AcOH	-1.21 <sup>b</sup>	8
(9) $(\text{CH}_3)_2\text{N}\cdot + \text{ArCH}_3$	136	$\text{C}_6\text{H}_6$	-1.08	25
(10) $\text{H}^+ + \text{ArCH}=\text{CH}_2$	25	$\text{H}_2\text{O}^d$	-3.42	26

<sup>a</sup> These figures are calculated from the data available in ref 4. <sup>b</sup> The figure is calculated from the data available in ref 8. <sup>c</sup> For these two  $\rho$  values better correlations were obtained with  $\sigma$  constants. For other  $\rho$  values,  $\sigma^+$  constants were used to give better correlation. <sup>d</sup> The reaction was run in 3.83 M aqueous  $\text{HClO}_4$  solution.

and established the general conditions for the competitive reaction of the piperidinium radical with styrenes.

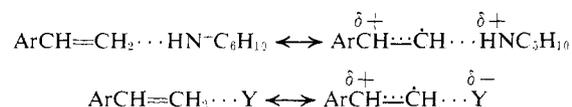
For the measurements of the relative reactivities, the competitive addition of the piperidinium radical was carried out in the presence of the standard substrate, styrene, and another meta- or para-substituted styrene. In each run the pseudo-first-order rate constants of the additions to styrene ( $k_{\text{H}}$ ) and that of the substituted styrene ( $k_{\text{X}}$ ) were calculated. The results are summarized in Table II. In the presence of *p*-methoxystyrene and styrene, nitrosamine photoaddition exclusively consumed *p*-methoxystyrene, while in the presence of *m*-bromostyrene and *p*-cyanostyrene, the former was exclusively attacked. These results unambiguously indicated that the aminium radical attack was electrophilic in nature and the relative reactivities in these couples were too far apart to be measurable experimentally. The reactivities of *p*-methoxystyrene were subsequently determined relative to *p*-methylstyrene and normalized to give  $k_{\text{X}}/k_{\text{H}}$  shown in Figure 1. The ratio  $k_{p\text{-CN}}/k_{\text{H}}$  was estimated to be <0.085 (see Experimental Section).

The distribution of the average of  $\log k_{\text{X}}/k_{\text{H}}$  along the  $\sigma$ -constant axis is shown in Figure 1. The reaction constant<sup>23</sup> ( $\rho$  value) computed by a least-squares method was -1.34 with  $r$  (correlation coefficient) = 0.978. When  $\sigma^+$  constants were used, the relative reactivities of *p*-methoxystyrene and, to a lesser extent, that of *p*-methylstyrene were much less than what could be predicted from other points. Relatively wider scatter of  $\rho\sigma^+$  relation could be seen when the  $\rho$  value of this distribution (excluding *p*-methoxystyrene) was computed by a least-squares method ( $\rho = -1.04$ ,  $r = 0.957$ ).

## Discussion

Polar effects of free radical reactions are principally governed by the electric requirements of the radical and the substrate, although secondary factors such as temperature and solvent no doubt also contribute significantly in some radical reactions.<sup>2,24</sup> It is expected that the presence of the positive charge in an aminium radical renders electrophilic character to this radical while

it is uncertain at what stage of the reaction coordinate this effect will be the greatest. It is suspected that reactions of this radical may have quite different electric requirements from those of neutral electrophilic radicals such as  $\cdot\text{Cl}$ ,  $\cdot\text{OC}(\text{CH}_3)_3$ ,  $\cdot\text{Br}$ , and  $\cdot\text{CCl}_3$ . For example, should a resonance effect be operative at the transition state, the addition to styrenes of the piperidinium radical induces dispersal of the cationic charge while that of a neutral radical ( $\text{Y}\cdot$ ) generates a partial charge separation.



In Table V some relevant  $\rho$  values are listed; for comparisons those of the dimethylamine<sup>25</sup> and the piperidinium radical hydrogen abstractions from toluenes<sup>8</sup> and of acid catalyzed hydration of styrenes<sup>26</sup> are also included. Although paucity of the data does not allow a systematic discussion of polar effects on radical addition reactions, the following observations can be mentioned. First, among the limited number of data available, the  $\rho$  value of the piperidinium radical addition is the largest and exhibits greater dependency on electron affinity than other neutral radical additions, although the comparisons with those using stilbene and  $\alpha$ -methylstyrene substrate systems have to be treated with caution. However, this  $\rho$  value is not exceptionally large when compared with that of the protonation of styrenes in which considerable positive charge density at the benzylic position is developed in the transition state.<sup>26</sup> Second, while all the neutral radical additions correlate better with  $\sigma^+$  constants, the piperidinium radical addition is a rare exception in which the relative reactivities exhibit better proportionality to the  $\sigma$  constants. The lack of correlation with the  $\sigma^+$  constant<sup>27</sup> is particularly obvious when the extremely electron donating and withdrawing *p*-methoxy- and *p*-cyanostyrenes are considered. Third, the present  $\rho\sigma$  relation is correlated by a single line for both para- and meta-substituted styrenes without showing enhanced reactivities for the para isomers as that observed in the trichloromethyl radical addition to styrenes.<sup>3</sup>

(23) The lowest  $k_{p\text{-Cl}}/k_{\text{H}} = 0.44$  in Table II appears abnormal but is included since we could not find any fault in the particular experiment. However, exclusion of this value does not make significant difference to the computed reaction constants; thus  $\rho = -1.31$  and  $r = 0.975$  when correlated with  $\sigma$  constants and  $\rho = -1.04$  and  $r = 0.970$  when correlated with  $\sigma^+$  constants excluding the *p*-methoxystyrene case.

(24) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963).

(25) C. J. Michejda and W. P. Hoss, *J. Amer. Chem. Soc.*, **92**, 6298 (1970).

(26) W. M. Schubert, B. Lam, and J. R. Reefer, *J. Amer. Chem. Soc.*, **86**, 4727 (1964).

(27) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

The unique features described above appear to be originated from the reaction mode rather than the attacking cationic radical species. A recalculation<sup>28</sup> of Neale's results<sup>8</sup> on the piperidinium radical abstraction from toluenes gives the relative reactivities better correlated with  $\sigma^+$  constants with a  $\rho$  value of  $-1.21$  which is smaller than those of the corresponding bromine atom and trichloromethyl radical abstraction reactions.<sup>2,8</sup> In comparison to that of the neutral dimethylamine radical abstraction<sup>25</sup> ( $\rho = -1.08$ ), this value is not noticeably larger. Our results suggest that in the piperidinium radical addition to styrenes the full C-N bond is developed at a very early stage and the benzylic carbonium ion character is not developed to any significant extent at the transition state. This is to be expected since the free energy of activation in this step is likely to be small in view of the high addition rate constant.<sup>13</sup> As a result, the substituent effects of styrenes through resonance at the transition state such as shown are minimal if not totally absent.<sup>27</sup> The substituents probably affect the electron density at the carbon-carbon double bond of the styrenes and thus the observed  $\rho$  value reflects the ground state electronic interaction between the cationic radical and the  $\pi$ -electron clouds. However, efforts to detect the presence of a charge-transfer complex between *p*-methoxystyrene and NNP by uv spectroscopy have not been successful. The conclusion arrived at above may be used to explain the failure of the NNP photoaddition to *n*-butyl vinyl ether. It is believed that the inductively electron-withdrawing butoxy group reduces the ground state electron density of the vinyl group even more than phenyl and retards the addition of the piperidinium radical.

As vastly different solvent systems are expected to modify the behavior of the piperidinium radical considerably, the Hammett correlation carried out in strongly acidic conditions, *e.g.*, 2 *M* H<sub>2</sub>SO<sub>4</sub> in AcOH, cannot be directly compared with that in the present conditions. Nor can the wide range of solvent systems

(28) Neale and Gross<sup>8</sup> have plotted  $\log \{[\text{XC}_6\text{H}_4\text{CH}_2\text{Cl}]/[\text{C}_6\text{H}_5\text{CH}_2\text{Cl}]\}$  against the  $\sigma^+$  constant by assuming a pseudo-zero-order reaction while  $k_X/k_H = \log \{([\text{XC}_6\text{H}_4\text{CH}_3]_0/[\text{XC}_6\text{H}_4\text{CH}_3]_t)/\log \{([\text{C}_6\text{H}_5\text{CH}_3]_0/[\text{C}_6\text{H}_5\text{CH}_3]_t)\}$  must be used.<sup>2</sup> As Dr. Neale informed us, their assumption would not cause a great deviation in the  $\rho$  value since their reactions are terminated at <30% conversions. This is indeed the case as demonstrated in the recalculated value using their published data.<sup>8</sup>

used in Table V be discussed meaningfully with the limited amount of data since the mode of solvation and effects of polarity, of hydrogen bonding, and of complex formations are not readily delineated.

Neale and Gross have implied their  $\rho$  value of the piperidinium radical abstraction as a minimum one on a basis of the various possible effects due to the high acidity medium; however, supporting evidence is lacking. Unfortunately, under strongly acidic conditions NNP is not photolabile due to the complete protonation of the nitrosamino group;<sup>14</sup> this prevents us from extending the present photoaddition study to a high acidity region. Photodecomposition of *N*-chloramine at a lower acidity region suffers from various side reactions<sup>8</sup> and is not readily adapted for a kinetic study. Recently Malatesta and Ingold<sup>29</sup> have demonstrated the increased stability of aminium radicals along with the increases in solvent acidity at the  $-H_0$  range of 3 to 11. Although the factors controlling the moderation of the reactivity are unknown, the aminium radicals are no doubt less reactive, and therefore more selective, at a higher acidity.

The quantum yield measurements indicate that the NNP photoaddition to styrene follows a short chain process with the chain length of about 6 to 10. The reasonable constancy of  $\phi_N$  in changing the styrene concentration indicates that every piperidinium radical reacts with styrene. Further the proposed mechanism is supported by the proportionality of  $\phi_N$  to the rate of propagation step ( $k_3$ ) as experimentally demonstrated by the increase of  $\phi_N$  along the increase in the NNP concentration. For this step to have an efficient rate, the energetic requirement must be that the activation energy is very small and certainly must be much smaller than that of the addition step. It is believed that styrenes and NNP form an oriented cluster in the solution probably regulated by electrostatic attraction of the reactants. The failure of detecting a charge-transfer absorption in a methanol solution of reactants may mean the interaction is not strong but not necessarily a negative proof.<sup>30</sup>

(29) V. Malatesta and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6400 (1973).

(30) It should be mentioned that nitrosamines do form oriented "collision complexes" with aromatic substances that are detectable by spectroscopy: see Y. L. Chow and C. J. Colón, *Can. J. Chem.*, **46**, 2827 (1968).