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Electrophilic Reactions of Xanthylium Carbocations Produced by Flash Photolysis of 9-Xanthenols

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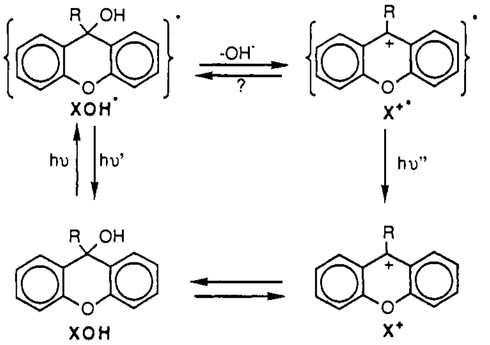
Abstract: The xanthylium ion and eight 9-aryl derivatives (*p*-MeO, *p*-Me, *m*-Me, H, *p*-F, *m*-MeO, *p*-Cl, and *p*-CF_3 phenyl) were produced in 1:4 acetonitrile/water by flash photolysis of the corresponding 9-xanthenols. The identifications of the transients as xanthylium cations were based upon their characteristic absorption spectra, as well as upon experiments with time-resolved conductivity detection. Rate constants for the reactions of these cations with solvent, with four anionic nucleophiles, and with four neutral nucleophiles (primary amines) were measured. The 9-arylxanthylium ions, which have solvent rate constants (k(solv)) at 25 °C ranging from 11 to 34 s^{-1}, follow the Ritchie equation, a plot of log k(nucleophile) versus the nucleophile N_+ parameter being linear with a slope near unity. For the more reactive parent cation, which has k(solv) at 20 °C of 2.3 × 10^4 s^{-1}, the rate constants k(nucleophile) are more poorly correlated with N_+ and the slope is less than unity. This is the second example of a reactive cation that fails to follow the Ritchie relationship. Possible explanations are that the rate constants are becoming diffusion-controlled or desolvation-controlled.

The implication that carbocations are intermediates of certain photosolvolysis and photohydration reactions[3] raises the possibility that with the use of time-resolved flash photolysis the lifetimes of the cations and their reactivities toward added nucleophiles can be directly measured under solvolytic conditions. The reactivities of very stable cations, whose reactions can be followed by conventional or stopped-flow spectroscopy, have been extensively studied,[4,5] but for less stable ions only indirect data are generally available.[6] Some triarylmethyl cations[7] and vinyl cations[8] have now been observed in flash photolysis experiments with appropriate precursors, and we have described a detailed study with the parent triphenylmethyl cation, generated from acetate and 4-cyanophenyl ether precursors.[9] Triphenylmethyl, diphenylmethyl, and even benzyl cations have been studied by pulse radiolysis,[10] but with this approach, the cations are generated in nonnucleophilic halocarbon solvents, and *not* in solvolytic media.

In this paper we report a study of xanthylium cations (X^+) generated photochemically in aqueous solution with xanthenol (XOH) precursors (eq 1). This system was suggested by the report of Wan, Yates, and Boyd that irradiation of 9-phenyl-9-xanthenol results in a weak fluorescence emission identical with that associated with the excited 9-phenylxanthylium ion.[11] This fluorescence was observed in neutral aqueous solutions where the amount of ground-state cation in equilibrium with the alcohol is extremely small. A strong fluorescence from the alcohol was also observed; the fluorescence spectrum for the cation was obtained in acid solutions where the ground-state equilibrium shifts to the cation side. Excitation of the neutral solution at 370 nm, a wavelength where the cation absorbs, produces no observable emission. The cation fluorescence at neutral pH therefore was argued to have originated from excitation of the alcohol, and a scheme (eq 1 with R = phenyl) was proposed whereby excited xanthenol undergoes heterolysis on the excited-state surface (adiabatic heterolysis) producing hydroxide ion and excited cation. Further evidence for this scheme came from photolysis in methanol, which showed a conversion of the alcohol to the methyl ether.[11]



(1)

The implication of these experiments is that photolysis produces an intermediate ground-state xanthylium ion. With the use of flash photolysis, we demonstrate that this is the case, not only for 9-phenyl but also for a series of 9-aryl derivatives and for the

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parent 9-unsubstituted system. We then go on to consider rate constants for the reactions of these ground-state cations with solvent and added nucleophiles. A preliminary account of the experiments with the parent xanthylium ion has been presented, in conjunction with our report of the flash photolysis generation of diarylmethyl and 4-methoxyphenethyl cations.[12] Boyd and Yates have recently demonstrated adiabatic cation fluorescence with our series of 9-(substituted phenyl)-9-xanthenols and with 9-xanthenol itself.[13]

Experimental Section

9-Phenyl-9-xanthenol and 9-xanthenol were commercially available and were recrystallized from ethanol/water before use. Other 9-aryl-9-xanthenols were prepared by addition of xanthone to an equivalent amount of the appropriate arylmagnesium bromide in ether. After 3–6 h refluxing, aqueous ammonium chloride was added, and the crude alcohols were obtained by separation of the ether phase, drying ($MgSO_4$), and removal of the ether. Purification involved flash column chromatography, followed by recrystallization, normally from ethanol/water. All compounds had appropriate ^1H NMR spectra and C,H analyses.

Photolysis experiments were carried out with a KrF excimer laser flash apparatus (20-ns flash width, λ = 248 nm), with optical and conductivity detection located at Mülheim, and with a conventional flash apparatus (50-μs flash width) with optical detection located at Toronto. The experimental setups and descriptions of data analyses have been reported elsewhere.[9,14] Solutions for the kinetic experiments were prepared by mixing in a 1:4 volume ratio doubly distilled water or water from a Millipore-Q system with spectroscopic grade acetonitrile, followed, after addition of the xanthenol and, where appropriate, nucleophile, by saturation with nitrogen or argon. Rate constants were obtained as the average of 4–6 kinetic runs carried out with each solution. The quantum yield experiments were carried out by preparing solutions of 9-phenyl-9-xanthenol and 9-xanthenol in 1:4 acetonitrile/water and potassium iodide in water, with the optical densities of all three at 1.02 ± 0.01 cm^{-1}. These solutions were sequentially loaded into the laser system, and for the same laser intensity, the transient optical density was measured immediately after the pulse, at wavelengths of 372 nm for the xanthenols and 650 nm for the iodide. Laser intensity was varied with neutral density filters.

Results and Discussion

Generation of Cations. The equilibrium constant, K_R = $[XOH][H^+]/[X^+]$, for ground-state 9-phenyl-9-xanthenol is 0.1,[11] so that a solution in 25% H_2SO_4 consists entirely of cation. The absorption spectrum recorded in this solution is shown by the solid line in Figure 1. The cation is characterized by a strong absorbance with λ_{max} at 372 nm with a weaker, broad absorption from 400 to 500 nm.

The 248-nm irradiation of 9-phenyl-9-xanthenol at pH 7, where the amount of cation present is extremely small, produces an absorbing transient (Figure 1) whose spectrum closely matches that obtained in the sulfuric acid solution. This transient is relatively long-lived, decaying with good first-order kinetics at 372 nm with a rate constant of 23 s^{-1}, at 25 °C and in a solvent 1:4 by volume acetonitrile/water. When acid solutions containing the 9-phenylxanthylium ion are neutralized in a stopped-flow spectrophotometer, a rate constant of 17 s^{-1} has been obtained for the decay of this ion, at 25 °C and an ionic strength of 0.3 in water.[15] Considering the different conditions, there is good agreement of this number with that obtained by flash photolysis. This also provides further evidence that the transient being observed after excitation is ground-state cation. The fluorescence lifetime of the excited 9-xanthylium ion in water is 0.15 ns,[11] so that the long-lived transient cannot be that species. In fact the steps leading from xanthenol to ground-state cation are complete within the 20-ns laser pulse, since the spectrum obtained at that time is that associated with ground-state cation as shown in Figure 1.

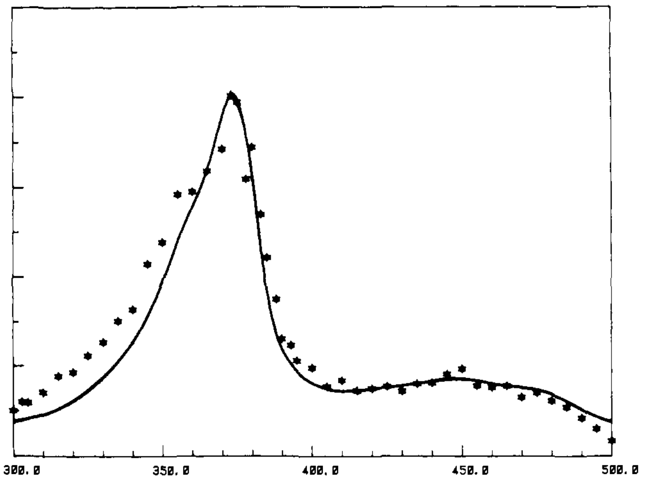

Figure 1. Transient absorption spectrum at 4–7 μs following 248-nm laser excitation (~20 mJ) of 0.1 mM 9-phenyl-9-xanthenol in argon-saturated 4:1 water/acetonitrile. The solid line is the spectrum of the 9-phenylxanthylium cation obtained by dissolving the alcohol in 25% H_2SO_4. This curve has been drawn such that it has the same absorbance as the transient at 372 nm. *x* axis, nm; *y* axis, OD.

A transient whose spectrum also matches that of authentic cation is produced upon excitation of the parent 9-xanthenol. This cation is considerably more reactive, decaying in 1:4 acetonitrile/water with a rate constant of 2.3 × 10^4 s^{-1}. Again there is good agreement with a previous number, 1.7 × 10^4 s^{-1}, determined using temperature-jump spectroscopy with equilibrating mixtures in acid solutions of the 9-xanthylium ion and 9-xanthenol.[16]

We also investigated a series of 9-phenyl-9-xanthenols substituted in the 9-phenyl ring (see Table I for substituents). Detailed spectra were not constructed, but in each case cation was observed upon excitation, based upon its characteristic 350–400-nm absorption.

Quantum yields for the formation of the parent and 9-phenylxanthylium ions were obtained by referencing the optical densities of these transients to that of the hydrated electron (e_{aq}^-) produced upon irradiation of an aqueous solution of iodide. In these experiments solutions of 9-xanthenol, 9-phenyl-9-xanthenol, and potassium iodide were irradiated under identical conditions (optical density at 248 nm, cell configuration and laser intensity), and the optical density was measured immediately after the pulse, at 372 nm for the cations and 650 nm for e_{aq}^-. As shown in Figure 2, the formation of the electron was linear in laser dose, while production of the xanthylium ions showed downward curvature. This is possibly an "inner-filter" effect[17] since the cations do absorb strongly at 248 nm and thus, once formed, can absorb the irradiating light in place of the alcohol. Quantum yields were calculated with eq 2[17] where S_X and S_e are the limiting slopes at zero

$$\phi(XOH \rightarrow X^+) = \left(\frac{S_X}{S_e}\right)\left(\frac{\epsilon_e}{\epsilon_X}\right)\phi(I^- \rightarrow e_{aq}^-) \qquad (2)$$

laser dose in Figure 2, and ϵ_X and ϵ_e are the extinction coefficients at the appropriate wavelengths of the electron and xanthylium ion, respectively. We used values of 1.64 × 10^4 M^{-1} cm^{-1} for ϵ_e (at 650 nm in water)[18] and 3.8 × 10^4 M^{-1} cm^{-1} (parent X^+) and 3.3 × 10^4 M^{-1} cm^{-1} (9-PhX^+) for ϵ_X, as measured for solutions of these cations in 20% $HClO_4$. The quantum yield for the formation of the hydrated electron was taken as 0.29, a value obtained by product analysis following 254-nm irradiation.[19]

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Table I. Rate Constants for the Reactions of 9-Substituted Xanthylium Ions with Solvent (s^{-1}) and with Added Nucleophiles ($M^{-1}\ s^{-1}$) at 25.0 °C in 1:4 Acetonitrile/Water

						primary amines RNH_2			
9-substituent	solvent	OH^-	CN^-	SO_3^{-2}	N_3^-	$CH_3CH_2CH_2$	$CH_3OCH_2CH_2$	$NCCH_2CH_2$	CF_3CH_2
4-$MeOC_6H_4$	1.1×10^1	2.6×10^4	7.9×10^3	8.9×10^6	8.8×10^7	1.6×10^5	6.3×10^4	1.9×10^4	1.9×10^3
4-MeC_6H_4	1.6×10^1	3.0×10^4	8.7×10^3	8.5×10^6	1.4×10^8	1.9×10^5	7.3×10^4	2.3×10^4	2.4×10^3
3-MeC_6H_4	1.9×10^1	3.4×10^4	1.0×10^4	1.0×10^7		1.8×10^5	7.6×10^4	2.4×10^4	2.2×10^3
C_6H_5	2.3×10^1	3.5×10^4	1.4×10^4	1.4×10^7	1.7×10^8	1.7×10^5	8.0×10^4	2.4×10^4	2.6×10^3
4-FC_6H_4	2.1×10^1	3.4×10^4	1.5×10^4	2.1×10^7	2.2×10^8	2.1×10^5	8.7×10^4	2.6×10^4	2.5×10^3
3-$MeOC_6H_4$	2.2×10^1	3.6×10^4	1.3×10^4	1.3×10^7	1.8×10^8	1.8×10^5	7.5×10^4	2.3×10^4	2.4×10^3
4-ClC_6H_4	2.7×10^1	7.2×10^4	2.1×10^4	2.0×10^7	3.0×10^8	2.5×10^5	1.1×10^5	3.1×10^4	3.0×10^3
4-$CF_3C_6H_4$	3.4×10^1		5.8×10^4	2.5×10^7	4.5×10^8	3.2×10^5	1.3×10^5		4.2×10^3
H[a]	2.3×10^4	3.5×10^7	8.0×10^6	1.6×10^9	6.3×10^9	2.8×10^7	2.6×10^7	2.0×10^7	6.6×10^6

[a] 20 ± 1 °C.

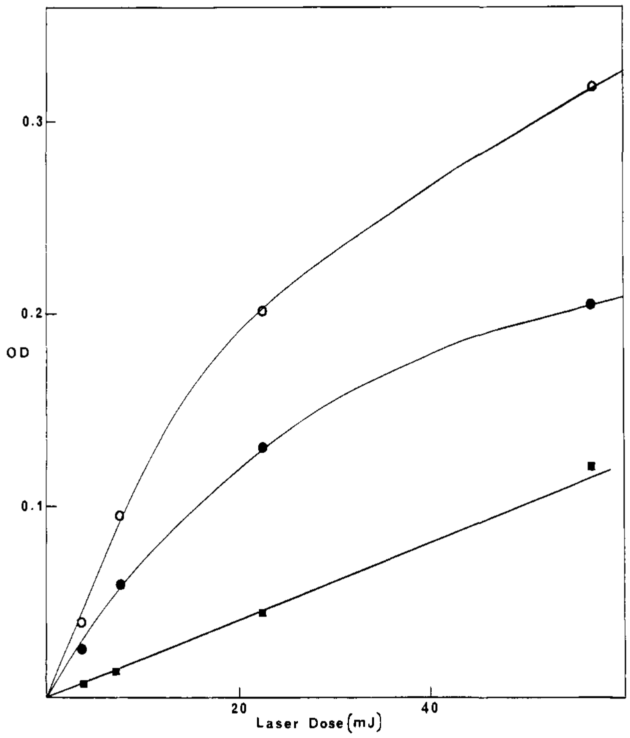


Figure 2. Optical density of transients as a function of 248-nm laser dose for the xanthylium ion (○) and the 9-phenylxanthylium ion (●) in 4:1 water/acetonitrile, both monitored at 372 nm, and the hydrated electron (■) in water, monitored at 650 nm.

Quantum yields thus calculated were 0.81 for the parent xanthylium ion and 0.56 for the 9-phenyl derivative. Considering the uncertainty in $\phi(I^- \rightarrow e_{aq})$ and the slightly different solvent used for obtaining ϵ_X, the error in these values could be ±0.1.

These quantum yields indicate very efficient photoheterolyses,[20] and this is interesting in a comparison with the previous investigation of the 9-phenyl compound, which found only a weak fluorescence for the cation produced adiabatically.[11] One explanation is that the quantum yield for adiabatic heterolysis of excited xanthenol is high, as measured in the flash photolysis experiments, but the majority of the excited cation so-produced decays to ground-state cation by nonradiative pathways. Boyd and Yates in fact have some recent evidence that this may be the case.[13] Experiments in which solutions of xanthylium ions are irradiated in aqueous H_2SO_4 of varying concentrations show that the fluorescence of the cation is quenched by water; extrapolation to pure water suggests that there will be only a weak fluorescence in that solvent. A second interpretation is that a fraction of the ground-state cation observed in the flash photolysis experiments does not arise out of excited-state cation but rather comes directly from excited alcohol in a process where deexcitation accompanies heterolysis.

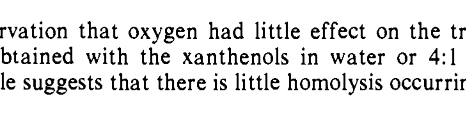
Quantum yields for the formation of the other 9-arylxanthylium ions were not measured. With one exception the optical densities of these transients were large, of similar orders of magnitude to the 9-phenylxanthylium ion, and thus the quantum yields are likely also quite high. The one exception was the *p*-trifluoromethyl derivative, which had a comparatively weak signal for the transient cation.

A close examination of Figure 1 reveals that there is additional absorbance at 300–350 nm not found in the spectrum of the 9-phenylxanthylium ion recorded in acids. Since the decay of optical density in this region was not accurately first-order, there must be some other transient species present. One clue as to the origin of this came from experiments with varying laser intensity. The transient spectrum obtained in Figure 1, for example, was obtained with 20 mJ of irradiating energy, using two 40% filters of the 248-nm light. When these were removed to increase the intensity to 125 mJ, the optical density was observed to increase at all wavelengths, as expected, but the match with the spectrum of the xanthylium ion was even poorer. There also appeared to be additional absorbance in the 400–500-nm region. This dependency on light intensity suggests that at least part of the extra absorbance is due to a species produced by a two-photon process, the probability of which increases with the square of the irradiating dose. A possible structure for this is the xanthenol radical cation or a reaction product derived from this. Radical cations can be produced in a two-photon process by photoionization.

$$XOH \xrightarrow{h\nu} (XOH)^* \xrightarrow{h\nu} (XOH)^{**} \rightarrow (XOH)^{\bullet +} + e_{aq}^- \quad (3)$$

Consistent with this explanation, experiments with 9-xanthenol at high laser intensities in pure water produced a weak spectrum at $\lambda > 500$ nm, which can be assigned to the hydrated electron. The hydrated electron could be completely scavenged by addition of O_2 to the solution. However, in the remaining spectral area at $\lambda < 500$ nm, there was relatively little difference in the spectra obtained in argon-saturated and oxygen-saturated solutions. Oxygen scavenges the electron, and organic radicals, but not radical cations[21] (or carbocations).

In our studies of diarylmethyl derivatives, photohomolysis producing radicals has been found to invariably compete with (and sometimes predominate over) photoheterolysis.[12,22]



$$Ar_2CHX \xrightarrow{h\nu} (Ar_2CHX)^* \begin{cases} \nearrow Ar_2C^+H + X^- \\ \searrow Ar_2\dot{C}H + X^\bullet \end{cases} \quad (4)$$

The observation that oxygen had little effect on the transient spectra obtained with the xanthenols in water or 4:1 water/acetonitrile suggests that there is little homolysis occurring upon

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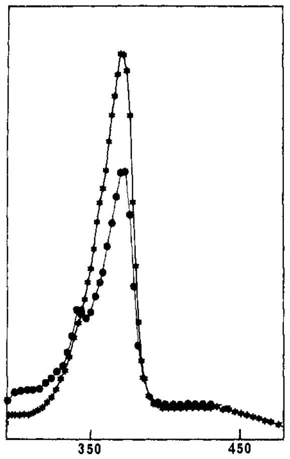

Figure 3. Transient absorption spectra at 4–6 μs following 248-nm laser excitation (~20 mJ) of 1.4 × 10^{-4} M 9-xanthenol in argon-saturated water and 1:3 water/acetonitrile. The trace in 100% water has the larger absorption at 372 nm: *x* axis, nm; *y* axis, OD.

irradiation of these species. However, when 9-xanthenol was irradiated in acetonitrile-rich solutions, there was observed a new transient, which absorbed at 345 nm (Figure 3) and reacted with oxygen. The nature of this transient, which is presumably a radical, is unknown. Figure 3 also shows a comparison of transient spectra in water and 1:3 water/acetonitrile obtained under identical conditions, and it is apparent that less cation is produced in the acetonitrile-rich solution. In pure acetonitrile, no cation signal was observed. This observation is consistent with the previous finding that there is no cation fluorescence when 9-phenyl-9-xanthenol is irradiated in acetonitrile.[11]

The production of cation was corroborated by experiments carried out with conductivity detection. Characteristic traces illustrating three different patterns of behavior are shown in Figure 4. Excitation in a weakly basic solution (curve B) results in a rapid conductivity increase, explained by the photoheterolysis producing charged species, the xanthylium ion and hydroxide ion. The conductivity then decreases to its original level as the cation is neutralized. In weak acids (curve A), the trace is the mirror image. Here, there is a rapid conductivity decrease upon excitation. This is caused by the neutralization of the hydroxide product of the photoheterolysis by the hydronium ion present. After this neutralization is complete, the solution contains xanthylium cation in place of an equivalent amount of hydronium ion and the conductivity has decreased since the organic ion is much less conducting. As the cation reacts with water, the hydronium ion is formed again and the conductivity rises. In both acids and bases, there is no overall change in the conductivity of the solution after the ground-state reaction of the cation with water, since there is no net photoreaction. A different situation, however, arises in a weakly basic solution containing azide ion. Excitation results in a conductivity increase very similar to that observed without the nucleophile, but with azide present, the decrease is faster and the conductivity does not return to zero. The explanation is that the cation is reacting with the powerful nucleophile azide rather than solvent, and there is thus a net photochemical reaction with azide being replaced in the solution by the more strongly conducting OH^-.

$$XOH \xrightarrow{h\nu} X^+ + OH^- \quad (5a)$$

$$X^+ + N_3^- \rightarrow XN_3 \quad (5b)$$

As one final point of corroboration, the slower conductivity changes, which occur after the laser pulse, were observed to obey excellent first-order kinetics, and the rate constants were, within experimental error, identical with those obtained in the same solutions following xanthylium ion decay optically at 372 nm. Finally, it can be noted that in each solution there is a transient pH increase[23] associated with the hydroxide ion released in the photoheterolysis.

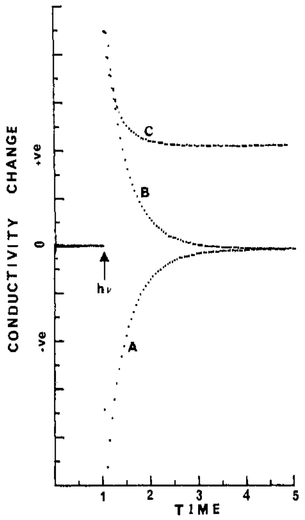

Figure 4. Conductivity changes following 248-nm excitation of 10^{-4} M 9-xanthenol in 4:1 water/acetonitrile: A, 10^{-4} M HCl, 160 ms/div; B, 10^{-4} M NaOH, 80 ms/div; C, 5 × 10^{-5} M NaN_3, 10^{-4} M NaOH, 10 ms/div.

The conductivity experiments with azide ion present also provide evidence that the rate accelerations that are observed are associated with the nucleophile combining with the xanthylium ion, as in eq 5b. The azidoxanthenol product is not stable, a feature which has been noted previously with both azido and amino adducts of stable triarylmethyl cations.[24] In the present case the instability is shown in the observation that the overall conductivity increase as in Figure 4 (curve C) is not permanent, but at very long times, there is a first-order return to the original conductivity level. This can be explained by the solvolysis of the azidoxanthenol-consuming hydroxide ion.

Electrophilic Reactivities. Table I lists the xanthylium ions studied in this work, their first-order rate constants *k*(solv) for decay in 1:4 acetonitrile/water, and their second-order rate constants *k*(Nu) for reaction with four anionic nucleophiles and four primary amines. Although there are large differences in reactivities in comparing the 9-unsubstituted xanthylium ion with the 9-aryl derivatives, the effect of the aromatic substituents in the latter turns out to be quite small. Figure 5 shows plots of five of the rate constants with the Hammett σ substituent constant. The ρ values range from +0.4 to +1.1, interestingly being somewhat higher for the anionic nucleophiles as compared to the neutral nucleophiles. A relative insensitivity to substituent has been previously noted with derivatives of Malachite Green[25] and in the present case can be related to two factors. The positive charge in these cations is undoubtedly highly delocalized in the xanthylium portion, and thus substituents on the 9-phenyl group will have a relatively small interaction with this, and thus a relatively small effect upon stability. Moreover, the 9-phenyl ring is likely to be twisted to some extent with respect to the plane of the three xanthylium rings, due to unfavorable steric interactions with the hydrogens at C1 and C8. This effect will decrease the conjugative interaction of para substituents.

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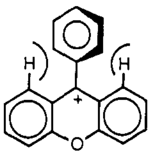

Ritchie has found that in their reactions with nucleophiles relatively stable triarylmethyl cations obey the relationship[4,5]

$$\log k = \log k_0 + N_+ \qquad (6)$$

where k is the second-order rate constant for the nucleophile-cation combination, k_0 is the rate constant for a reference nucleophile, and N_+ is a nucleophilicity parameter dependent only upon the nucleophile and solvent. This relationship is an example of the failure of the reactivity/selectivity principle, since it shows a constant selectivity with changing reactivity. Suggestions have been made that a selectivity parameter should be included[26] but Ritchie has argued that this is unnecessary with the experimental scatter in the measurements.[27]

The Ritchie equation predicts that a plot of log k versus N_+ should be linear and moreover that the slope should be unity. Such plots are drawn in Figure 6 for the parent xanthylium ion and the 9-phenylxanthylium ion. The other 9-arylxanthylium ions behave very similarly to the latter with just a slight displacement in the vertical direction. The plot for the 9-phenylxanthylium ion clearly does take the required form. There is some scatter, but the slope, ignoring the solvent point for reasons discussed by Ritchie,[5] is 0.97. The more reactive parent, however, shows more scatter, and moreover the slope of the plot is only 0.65. The 9-phenylxanthylium ion, with a solvent rate constant of 23 s^{-1}, is similar in reactivity to the tris(p-methoxyphenyl)methyl cation, k(solv) = 12 s^{-1}.[24,26,28] The latter is the most reactive cation included in the Ritchie analysis[4,5] and does adhere reasonably well to the equation. We have previously found that the parent triphenylmethyl cation, with k(solv) = 1.5×10^5 s^{-1}, has log k(Nu) roughly linear in N_+, but with a slope of only 0.4.[9] The parent xanthylium ion thus fits the same pattern, a more reactive cation with a slope less than unity in the N_+ plot.

Figure 7 depicts this behavior in a slightly different way, in terms of a linear free energy correlation involving the reactions of various cations referenced to the 9-phenylxanthylium ion. The 9-arylxanthylium ions and the tris(p-methoxyphenyl)methyl cation show good linear correlations, with slopes near unity. The two more reactive ions, however, produce lines with more scatter and slopes significantly less than unity. A corollary of the Ritchie equation is that log k for a given cation should be linear in log k for a second, and moreover the slope should be unity.

The data shown in Figure 8 indicate one source of the deviation for the more reactive cations. This figure graphically represents the change in the rate constant for reaction with azide as the cation reactivity is increased, using the rate constant for reaction with solvent as a measure of the latter. Data for more reactive diarylmethyl cations are also included in this figure. For the five more reactive of these k(azide) is 7×10^9 M^{-1} s^{-1} in spite of a 30-fold increase in k(solv). We have argued that this indicates that the reaction of azide with these cations is diffusion-controlled,[12] a situation which had been suspected for reactive cations but not directly proven.[6c,29] The 9-arylxanthylium ions are clearly reacting with azide with a rate constant that is significantly below this limit, and increases in k(solv) are accompanied by increases in k(azide). The parent xanthylium ion, on the other hand, has k(azide) = 6.3×10^9 M^{-1} s^{-1}, very close to the limit. With this nucleophile therefore, the Ritchie equation must break down, since

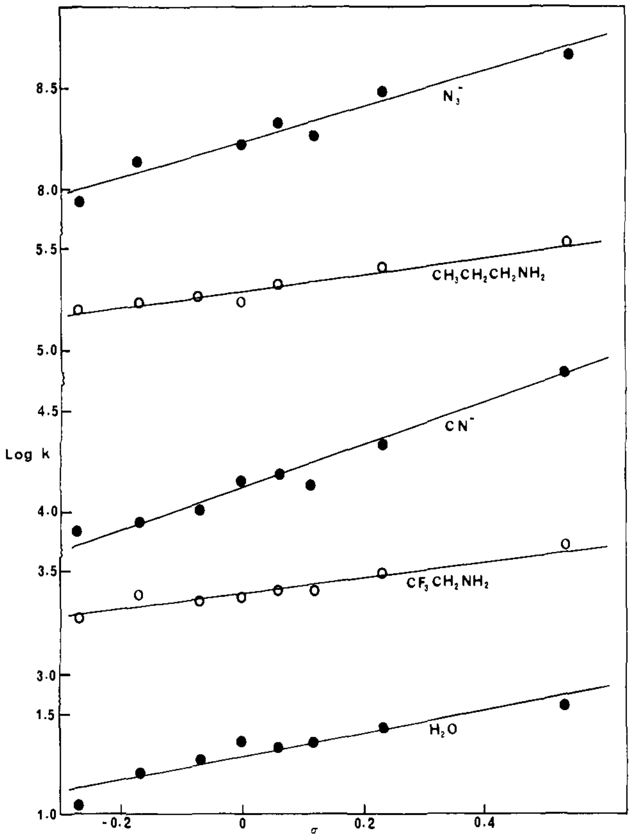

Figure 5. Hammett plots for 9-arylxanthylium ions. Lines are based upon linear regression and have slopes (ρ) of +0.5 (solv), +0.4 ($CF_3CH_2NH_2$), +1.0 (CN^-), +0.4 ($CH_3CH_2CH_2NH_2$), and +0.8 (N_3^-).

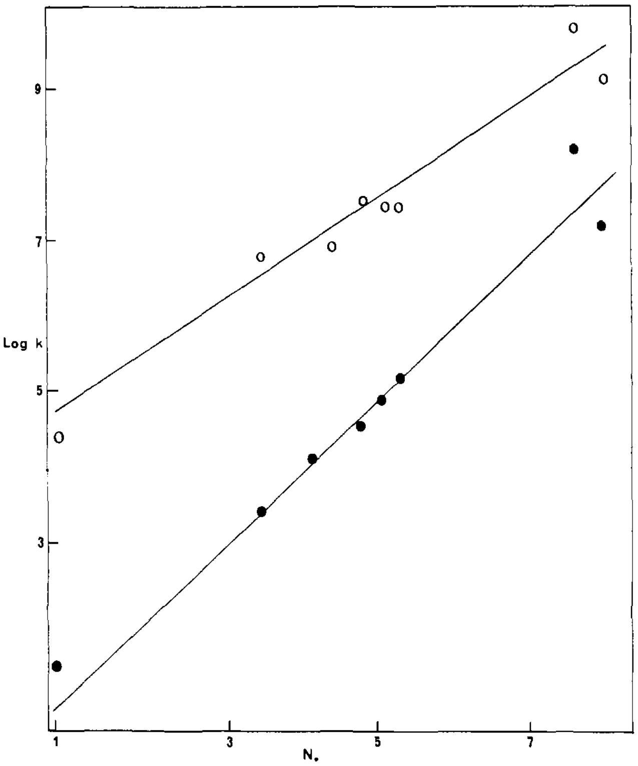

Figure 6. N_+ correlations for reactions of the xanthylium ion (○) and 9-phenylxanthylium ion (●) with nucleophiles. Lines drawn are based upon linear regression ignoring the solvent point and have slopes of 0.97 (○) and 0.65 (●).

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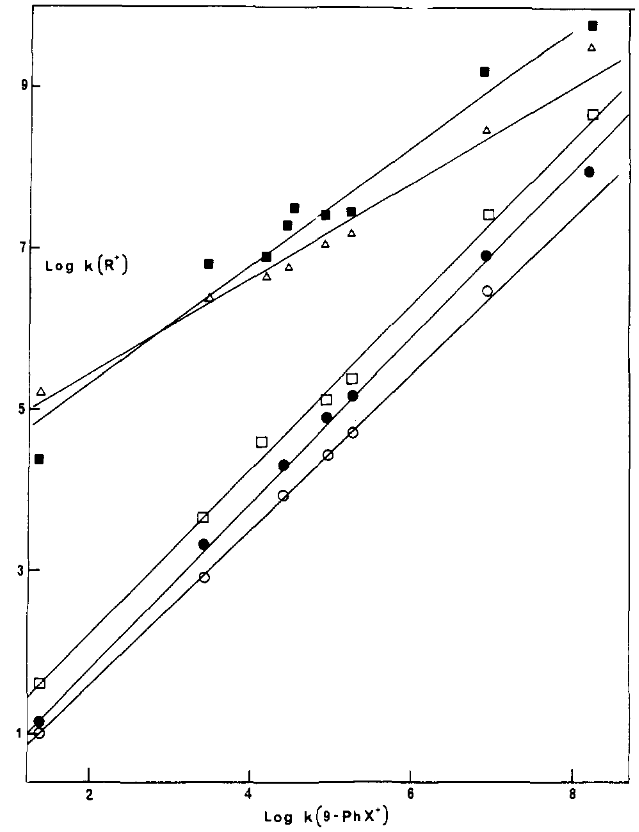


Figure 7. Linear free energy correlations. Cations and linear regression slopes are the following: (○) tris(*p*-methoxyphenyl)methyl, 0.94; (●) 9-(*p*-methoxyphenyl)xanthylium, 1.00; (□) 9-[*p*-(trifluoromethyl)phenyl]xanthylium, 1.02; (■) xanthylium, 0.75; (△) triphenylmethyl, 0.61. The reference cation is the 9-phenylxanthylium ion.

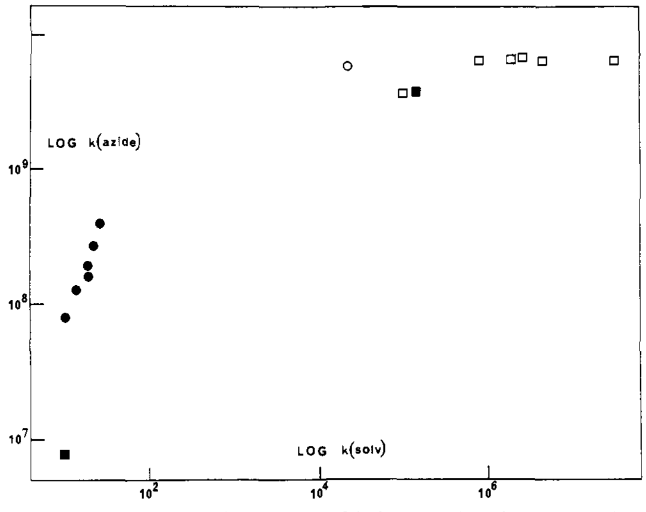


Figure 8. Dependence of *k*(azide) on *k*(solv): (●) 9-arylxanthylium ion; (○) xanthylium ion; (■) tris(*p*-methoxyphenyl)methyl[24] and triphenylmethyl[9] cations; (□) diarylmethyl cations.[12]

the rate constant is not determined by reactivity factors but mainly by diffusion.

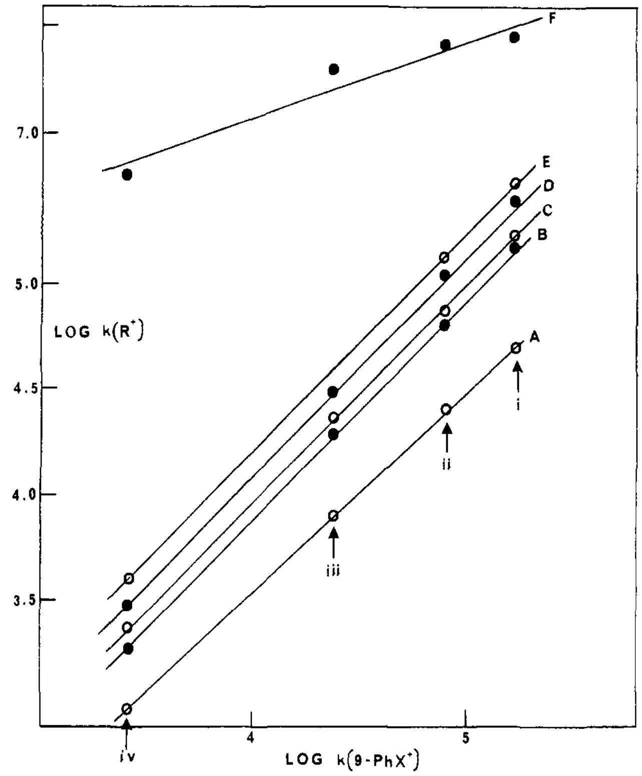
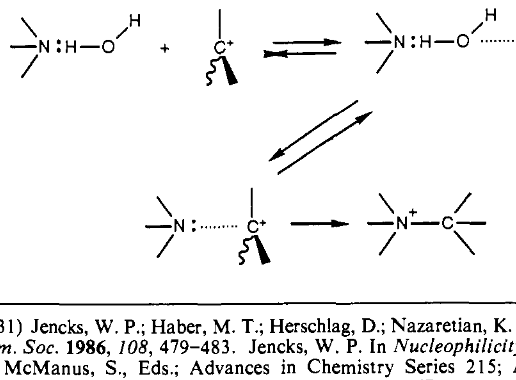


Figure 9. Linear free energy correlations for primary amines: (i) $CH_3CH_2CH_2NH_2$; (ii) $CH_3OCH_2CH_2NH_2$; (iii) $CNCH_2CH_2NH_2$; (iv) $CF_3CH_2NH_2$. Cations and linear regression slopes: A, tris(*p*-methoxyphenyl)methyl, 0.94; B, 9-(*p*-methoxyphenyl)xanthylium, 1.02; C, 9-(*p*-methylphenyl)xanthylium, 1.01; D, 9-(*p*-chlorophenyl)xanthylium, 1.03; E, 9-[*p*-(trifluoromethyl)phenyl]xanthylium, 1.01; F, xanthylium, 0.36. The reference cation is the 9-phenylxanthylium ion.

Ritchie has predicted that as the diffusion limit is reached there should be a sharp break in the plot of log *k* versus N_+, with the slope changing from unity to zero,[4] and there are examples of such behavior.[4,30] It is questionable however whether the xanthylium ion actually follows this pattern, since even for those nucleophiles that react significantly below the 10^{10} limit, a line with a slope less than unity provides a better fit. A possible explanation for this breakdown can be seen in the data for the four primary amines. These are plotted in Figure 9 as linear free energy correlations, referenced to the 9-phenylxanthylium ion. A good linear correlation is observed with the other 9-arylxanthylium ions, and with the tris(*p*-methoxyphenyl)methyl cation, with slopes near unity. Thus the sensitivity of these other cations to changing amine nucleophilicity is very similar to that of the 9-phenylxanthylium ion. However, when the data for the parent xanthylium ion are considered in the same fashion, not only is the slope of the correlation less than unity but, more importantly, the plot shows curvature. The two most basic amines, propylamine and 2-methoxyethylamine, react with a similar rate constant with the parent xanthylium ion but differ by a factor of 2.5 in their reactions with the 9-arylxanthylium ions. The next most basic amine, 2-cyanoethylamine, is slightly less reactive toward the xanthylium ion, but the factor is small. There is then a larger decrease with the least basic amine, 2,2,2-trifluoroethylamine.

Jencks has argued that an important component in the consideration of the reactivity of amines and oxyanions is desolvation.[31]



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J. Am. Chem. Soc. 1989, 111, 2935-2946

The situation can arise with a reactive electrophile where the actual combination step is very fast, but the requirement for desolvation limits the reaction. This can appear experimentally as an inversion of the normal nucleophilicity order, a more basic amine being less reactive because it is more strongly solvated. There is a recent report based upon amine/azide selectivities illustrating such behavior.[32] The parent xanthylium has not quite reached this point in its reactivity. The curvature in the correlation with the less reactive cations indicates however that desolvation is partially limiting, particularly for the more basic amines. The consequence again is that the simple Ritchie relationship is unlikely to apply.

In summary the parent xanthylium ion provides a second example of a reactive cation where the N_+ relationship is not obeyed in its simple form. This nonadherence is likely to be a general situation for cations that are not highly stabilized, or, in other words, the Ritchie relation may be a special case describing the behavior of only strongly stabilized cations.

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Making Mercury-Photosensitized Dehydrodimerization into an Organic Synthetic Method: Vapor Pressure Selectivity and the Behavior of Functionalized Substrates

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Abstract: Mercury-photosensitized dehydrodimerization in the vapor phase can be made synthetically useful by taking advantage of a simple reflux apparatus (Figure 1), in which the products promptly condense and are protected from further conversion. This vapor pressure selectivity gives high chemical selectivity even at high conversion and on a multigram scale. Mercury absorbs 254-nm light to give the $^3P_1$ excited state (Hg*), which homolyses a C-H bond of the substrate with a 3° > 2° > 1° selectivity. Quantitative prediction of product mixtures in alkane dimerization and in alkane-alkane cross-dimerizations is discussed. Radical disproportionation gives alkene, but this intermediate is recycled back into the radical pool via H atom attack, which is beneficial both for yield and selectivity. The method is very efficient at constructing C-C bonds between highly substituted carbon atoms, yet the method fails if a dimer has four sets of obligatory 1,3-syn methyl-methyl steric repulsions, as in the unknown 2,3,4,4,5,5,6,7-octamethyloctane. We have extended the range of substrates susceptible to the reaction, for example to higher alcohols, ethers, silanes, partially fluorinated alcohols, and partially fluorinated ethers. We see selectivity for dimers involving C-H bonds α to O or N and for S-H over C-H. An important advantage of our experimental conditions in the case of alcohols is that the aldehyde or ketone disproportionation product (which is not subject to $H^\bullet$ attack) is swept out of the system by the stream of H_2 also produced, so it does not remain and inhibit the rate and lower the selectivity. k_{dis}/k_{rec} is estimated for a number of radicals studied. The very hindered 3° 1,4-dimethylcyclohex-1-yl radical is notable in having a k_{dis}/k_{rec} as high as 7.1.

We have long been interested in alkane functionalization.[1,2] In connection with this problem, we have now developed mercury-photosensitized dehydrodimerization[3] as a synthetically useful method both for alkanes and for other substrates. In this paper we describe an apparatus which makes this method practical for use on a multigram scale. In order to understand the results, we also carried out mechanistic work on the radical pathways which occur in this system.

The method addresses a general problem in alkane functionalization: the products are generally more reactive than the alkane substrates, and so it has previously been necessary to keep the conversion very low to prevent "double hits" on the same molecule by the necessarily very reactive alkane-conversion reagent. Low conversion not only introduces separation problems but also prohibits the use of valuable substrates.

We show in this paper how mercury photosensitization can be made preparatively useful for dehydrodimerization by selective, stoichiometric radical recombination by adopting an experimental setup in which the product is protected by prompt condensation. This "vapor pressure selectivity" allows us to obtain both *high selectivity and high conversion at the same time.* The potential problems which might have been caused by disproportionation of the radicals is mitigated for the alkane substrates by $H^\bullet$ atom addition to the alkene disproportionation product and for alcohol substrates by sweeping the aldehyde or ketone disproportionation product out of the reactor. In a second paper, which follows this one, we show that compounds of different classes (e.g., alkanes and alcohols) can be cross-dehydrodimerized and that the cross-dimer can be easily separated. This constitutes a general and effective *alkane functionalization which is applicable to large-scale work.* Some of this work has appeared in communications[4,5] and in a patent.[6]

Mercury-photosensitized dehydrodimerization (eq 1) has been known since the pioneering work of Hill[7a] and Steacie[7b] in the 1920s and 1930s and was intensively studied in the period

$$2\text{R-H} \xrightarrow{\text{Hg}^*} \text{R-R} + \text{H-H} \qquad (1)$$

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