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Ion-Pair Recombination of a Carbocation and Hydroxide Ion Observed in Solvolytic Media by Laser Photolysis of 9-Aryl-9-xanthenol[1)]

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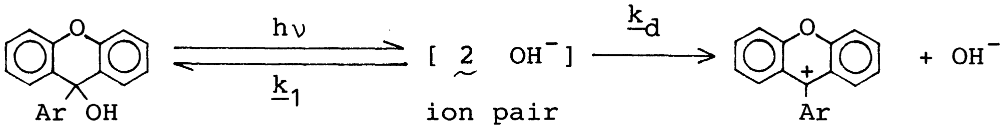
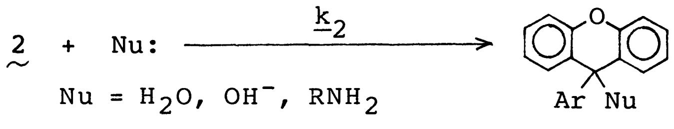
9-*p*-Methoxyphenyl-9-xanthenylium ion is generated by laser photolysis of the corresponding xanthenol in aqueous ethanol. The time-dependent absorbance change shows a biphasic first-order decay with halflives of 10^{-4} and 10^{-2} s. The rapid reaction is ascribed to the ion-pair recombination.

Ionization of organic compounds is an important step of S_N1 solvolysis reactions. Ions formed exist as ion pairs or free ions in reaction media.[2)] Behavior of ion pairs has been looked into indirectly by solvent and salt effects on the reaction. Rates for recombination of ion pairs are hard to be evaluated by usual techniques. Some reversible ionizations of organic halides and similar derivatives were examined by the dynamic NMR method.[3,4)] In order to see the recombination of ion pairs by this method, the ion pairs should necessarily be present by appreciable fractions in equilibrium, and hence the substrates are limited to those which produce very stable ions and solvents should be non-reacting ones. The present communication describes the first direct observation of recombination of the ion pair of a carbocation and hydroxide ion in protic solvents relevant for solvolysis reactions.



(1)

1, Ar = p-$MeOC_6H_4$ 2



(2)

9-(p-Methoxyphenyl)-9-xanthenylium ion (**2**) was generated in aqueous ethanol by photolysis of the corresponding alcohol (**1**)[5] with an Nd:YAG laser pulse operated at 266 nm.[6] The transient spectra obtained at 10-100 μs after a laser pulse show λ_{max} at ca. 370 nm in accord with those observed in strong acid. Similar observations have recently been reported.[8,9] The absorption at 345 nm which is ascribed to a xanthenyl radical[8,9] was also observed.

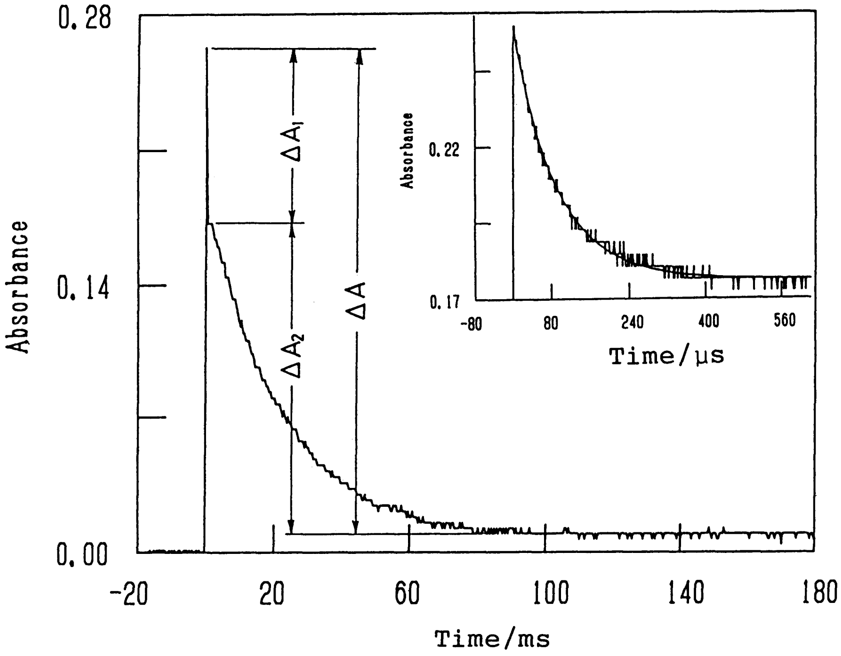


Fig. 1. A biphasic absorbance change in 50 vol % aqueous ethanol (μ = 0.10). The insert shows the rapid decay with the first-order curve.

The decay of the 370 nm absorption is biphasic with rapid and slow phases as shown in Fig. 1.[10] Both the rapid and slow reactions typically follow the pseudo-first-order kinetics, but the rapid phase becomes complex (decaying more rapidly than the first-order curve) in the presence of added hydroxide ion or in less polar media (>50 vol % ethanol). The first-order rate constants, k_1 and k_2,[11] determined in aqueous ethanol for the rapid and slow reactions are summarized in Table 1 together with absorbance changes ΔA observed during the reaction. The rate constants k_1 are given as approximate values obtained by fitting the whole curve to a calculated first-order curve even if fitting is very poor (shown in parentheses). The transient absorption in the 370 nm region is not affected by bubbling with Ar or O_2.

The k_2 for the slow reaction are essentially the same as those obtained by the conventional xenone-lamp flash photolysis[1] and in accord with those reported by McClelland,[8] increasing with increasing concentration of added nucleophiles. The reaction is ascribed to trapping of the free ion **2** by external nucleophiles (solvent or added nucleophiles).

On addition of a small amount of acid, the rapid reaction is quenched and the absorbance change for the slow one increases while k_2 is little influenced (No. 5). This observation is best accommodated by the assumption that the rapid reaction is recombination of the ion pair of **2** and hydroxide

Table 1. Rate Constants and Absorbance Changes for the Decay of **2** Measured by Laser Photolysis in Aqueous Ethanol[a]

No.	Vol% H_2O	Additive(concn/M[b])	μ[c]	$10^{-4}k_1$[d]/s^{-1}	$10^{-2}k_2/s^{-1}$	%$\Delta A_1(\Delta A)$[e]
1	50	none	0.1	1.16	0.55	46 (0.26)
2	50	OH^- (10^{-4})	0.1	(1.3)	0.57	50 (0.27)
3	50	OH^- (10^{-3})	0.1	(2.0)	5.3	72 (0.27)
4	50	RNH_2[f] (10^{-3})	0.1	(1.7)	0.97	64 (0.30)
5	50	$HClO_4$ (10^{-3})	0.1	not obsd	0.51	0 (0.28)
6	20	OH^- (10^{-4})	0	(3.3)	2.9	67 (0.15)
7	40	OH^- (10^{-4})	0	(2.8)	1.2	62 (0.21)
8	50	OH^- (10^{-4})	0	(3.0)	0.74	56 (0.25)
9	60	OH^- (10^{-4})	0	3.3	0.61	49 (0.30)
10	80	OH^- (10^{-4})	0	6.7	0.34	34 (0.44)
11	50	OH^- (10^{-4})	0.5	0.84	0.43	39 (0.34)

a) Monitored at 370 nm at 25 ± 2 °C. b) 1 M = 1 mol dm^{-3}. c) Ionic strength maintained with $NaClO_4$. d) Values in parentheses are approximate overall rate constants. e) ΔA and ΔA_1 are absorbance changes due to the whole reaction and the rapid one, respectively. f) R = $MeOCH_2CH_2$.

ion. Acid can rapidly (at the diffusion-controlled rate) trap the pairing hydroxide to destroy the ion pair affording the free ion **2** but can little affect the reaction of **2** with the nucleophilic solvent(k_2). The spectrum of the ion pair is assumed essentially to be identical with that of the free ion as the transient spectra show.

The rate constant k_1 for the recombination and k_d for the dissociation of the ion pair to the free ions should be similar in magnitude. The dissociation process is however not visible since the absorption at 370 nm does not change. The observed absorbance change ΔA_1 due to the rapid reaction and ΔA_2 due to the slow reaction must correspond respectively to the recombination and dissociation of the ion pair: $\Delta A_1/\Delta A_2 = k_1/k_d$. The reverse of dissociation is usually slow enough for the formed free cation to undergo the slow reaction with nucleophiles because the concentration of free hydroxide ion is very low. However, in the presence of added hydroxide ion, the association process may become unable to be neglected. As a microscopic reverse, the slow reaction of the free carbocation with an anionic nucleophile should involve formation of an ion pair.

With an increase in water content of the solvent, the total absorbance change ΔA increases while the percent absorbance change due to the rapid reaction ΔA_1 decreases (No. 6-10). That is, the quantum yield of heterolysis of **1** increases with increasing polarity of the medium, while the rate of dissociation k_d may increase owing to the decreasing Coulombic interaction and hence the values of k_1/k_d become smaller. Similar effects on the absorbances were also found on addition of the salt, $NaClO_4$ (No. 2, 8, 11). The k_2 decreases with increasing content of water while the k_1 is only slightly affected. Both solvent and salt effects on k_2 are reasonable for reaction of a free ion which will be stabilized in more polar media. However, the effects on k_1 are not straightforward and remain to be clarified. Non-first order nature of the rapid decay seems to suggest existence of multiple states of the ion pair having different decay rates. More examples of this kind of measurements are needed to discuss about further details of the ion-pair process. Examinations on substrates carrying a different nucleofuge and conductometric measurements are considered.

References

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3) H. Kessler and M. Feigel, Acc. Chem. Res., 15, 2 (1982) and references therein.
4) M. Oki, Pure Appl. Chem., 61, 699 (1989) and references therein.
5) A sample of **1** was prepared by the Grignard reaction of 9-xanthenone and *p*-bromoanisole.
6) A Q-switched Nd:YAG laser (Quantaray DCR-2) operated by the fourth harmonic generation (60 mJ, 6 ns fwhm) was used for laser photolysis.7)
7) Y. Morishima, T. Kobayashi, T. Furui, and S. Nozakura, Macromolecules, 20, 1707 (1987).
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9) R. E. Minto and P. K. Das, J. Am. Chem. Soc., 111, 8858 (1989).
10) McClelland and coworkers analyzed closely the slow reaction without mentioning the rapid phase of the reaction,8) while Minto and Das only briefly mentioned the complexity of the decay curve.9)
11) The k_2 are given as observed pseudo-first-order rate constants since nucleophiles are always present in large excess.

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