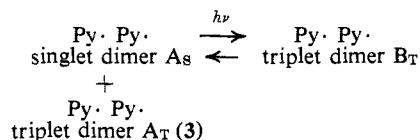Figure 1. Epr spectra of 4-carbomethoxy-1-methylpyridinyl in MTHF glass at 77°K, before (a) and after (b) the irradiation of visible light; $c = 3.8 \times 10^{-2} M$. Gain ratio for three curves = 1:45:207.
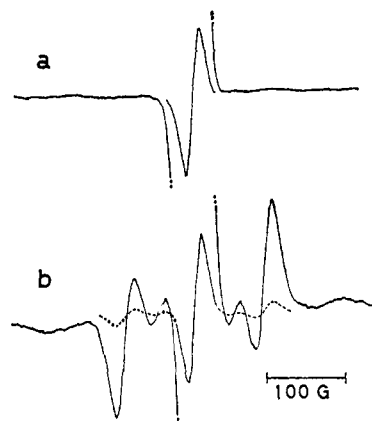

Figure 2. Epr spectra of 4-carbomethoxy-1-methylpyridinyl with sodium iodide in MTHF at 77°K, before (a) and after (b) the irradiation of visible light; $c = 5.0 \times 10^{-2} M$. Gain ratio for two curves = 1:10.

symmetrical arrangement than that of A_T form. The D value is consistent with a spin–spin dipolar interaction for an average separation of 5.4 Å.

It is believed that the second triplet state, B_T, was generated by an excitation–relaxation sequence from the diamagnetic dimer (A_S form), since the signal intensity at the $g = 2$ region did not vary after the irradiation. The generation occurred with visible light in the region of 420–500 nm, implying that the excitation responsible for the formation of B_T is not the long-wavelength charge-transfer absorption at around 620 nm.[1] The long lifetime of the B_T signal proves that the energy $^3\Psi_0$ of B_T state is close to the energy $^1\Psi_0$ of the A_S state.[6]

We can thus postulate several kinds of radical pairs for the radicals in MTHF glass. The diamagnetic radical pair A_S coexists with the randomly oriented radical pair A_T which exhibits triplet transitions. Light irradiation generates another triplet dimer B_T from the diamagnetic dimer.

$$\begin{array}{ccc} \text{Py} \cdot \text{Py} \cdot & \xrightarrow{h\nu} & \text{Py} \cdot \text{Py} \cdot \\ \text{singlet dimer } A_S & \longleftarrow & \text{triplet dimer } B_T \\ & + & \\ & \text{Py} \cdot \text{Py} \cdot & \\ & \text{triplet dimer } A_T \text{ (3)} & \end{array}$$

Sodium iodide acts on the radicals so as to favor the dimerization. A difference in the epr spectrum of the β solution from that of the α solution could be explained by specific complex formation of a pyridinyl radical with sodium iodide such as those formed by a π mer.[7] The longest wavelength band of the β solution at 77°K appeared at 608 nm, shifted 45 nm to shorter wavelength from that of the α solution. The complex formation is shown directly through the fact that deep blue crystals with the composition $(\text{Py} \cdot)_2\text{NaI}$ separate on cooling the β solution to $-76°$ at a moderate concentration. A similar salt effect on radical association was observed with lithium iodide, but no triplet signal appeared on irradiation at 77°K. No effect of potassium iodide on the radical association has been observed. Thus, the sodium cation seems to assist the

(6) N. Mataga and T. Kubota, "Molecular Interaction and Electronic Spectra," Marcel Dekker, New York, N. Y., 1970, p 275.

(7) E. M. Kosower and J. Hajdu, J. Amer. Chem. Soc., 93, 2534 (1971).

formation of the singlet radical dimer convertible into the triplet dimer by light irradiation.

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Cation–Anion Combination Reactions. X. General Base Catalysis in the Reaction of a Carbonium Ion with Water

Sir:

Reported here is the direct observation of general base catalysis of the reaction of a carbonium ion with water, which also requires that the reverse reaction, formation of carbonium ion from alcohol, is subject to general acid catalysis. In all previous work, reactions of this type were believed to involve specific acid–base catalysis only.

Data for the reaction of Malachite Green cation (bis(p-dimethylaminophenyl), phenylmethyl cation) in aqueous solutions buffered with Dabco (diazabicyclo-[2.2.2]octane) and its conjugate monoacid are reported in Table I. The reactions were followed by observing the absorbance of the reaction solutions at 623 nm, using a 10.0 cm cell path, as a function of time. At the pH used in these studies, 8.78 ± 0.02, the contribution to the observed rate from the reaction of hydroxide ion is less than 1.4×10^{-5} sec^{-1} (i.e., $k_{OH} = 2.18$ M^{-1} sec^{-1}),[1] and the slight variation in pH has a negligible effect on the observed rates.

A plot of the pseudo-first-order rate constants vs. the concentration of Dabco is shown in Figure 1. The line shown in the figure gives k_{Dabco}, the second-order rate constant for catalysis by Dabco, as 2.6×10^{-3} M^{-1} sec^{-1}, and $k_{H_2O} = 2.08 \times 10^{-4}$ sec^{-1}. The latter value is in excellent agreement with our previous determinations.[1]

(1) C. D. Ritchie, G. A. Skinner, and V. G. Badding, J. Amer. Chem. Soc., 89, 2063 (1967).
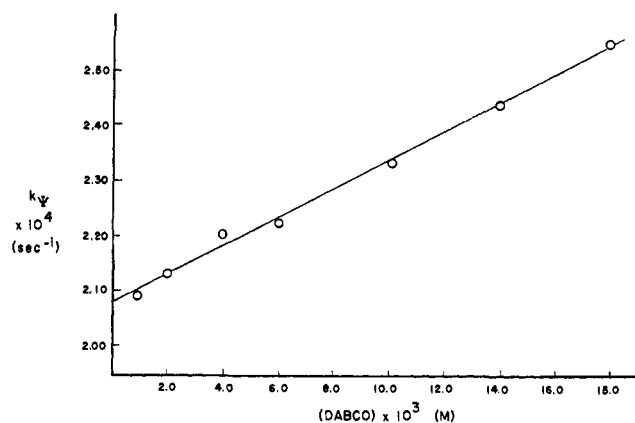
Figure 1. Dependence of the observed pseudo-first-order rate constant on amine concentration for the reaction of Malachite Green with water.

In our earlier work,[1] we utilized triethylamine–triethylammonium ion buffers at concentrations of less than 10^{-3} M. We remarked that the observed rates appeared to depend on buffer concentration at higher concentrations than those reported, but attributed the

Table I. Reaction of Malachite Green with Water at $25.0 \pm 0.1°$[a]

[Dabco], M	pH[b]	k_{obsd}[c] $\times 10^4$
1.0×10^{-3}	8.767	2.09
2.0×10^{-3}	8.775	2.13
4.0×10^{-3}	8.789	2.20
6.0×10^{-3}	8.803	2.22
1.0×10^{-2}	8.783	2.33
1.4×10^{-2}	8.778	2.44
1.8×10^{-2}	8.776	2.55

[a] The initial concentration of Malachite Green fluoroborate was 1.23×10^{-6} M in all experiments. Ionic strength was maintained constant at 1.8×10^{-2} M by addition of the required amount of potassium perchlorate. Buffers were prepared by half-neutralization of Dabco with perchloric acid. [b] The pH of the reaction solution was measured at the beginning and end of each kinetic run with a Beckman Model 1019 pH meter standardized with a commercial pH 6.865 buffer. [c] Pseudo-first-order rate constant in units of sec^{-1}.

effect to primary and secondary amine impurities in the buffer. The recent work by Bruice[2] and experiments with reactions of ethylamine and diethylamine in our laboratories[3] show that the equilibrium constants for the reactions of Malachite Green with amines are so small that even substantial amounts of such impurities in the buffers would cause negligible effects on the rates of the reactions. A reexamination of our data at relatively high buffer concentrations (10^{-2}–10^{-1} M) gives a value of 3×10^{-2} M^{-1} sec^{-1} for the second-order rate constant for catalysis of the reaction by triethylamine.

The pK values of the conjugate acids of Dabco and triethylamine are 8.8[4] and 10.8,[5] respectively. The rate constants given above lead to a Brønsted coefficient of ca. 0.5 for the base catalysis. Use of the pK value of

(2) J. E. Dixon and T. C. Bruice, J. Amer. Chem. Soc., 93, 3248 (1971).
(3) This work by Dr. P. O. Virtanen is the subject of a paper in preparation.
(4) P. Paoletti, J. H. Stern, and A. Vacca, J. Phys. Chem., 69, 3759 (1965).
(5) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p 65.

15.74 for water leads us to expect the rate constant for catalysis by hydroxide ion to be ca. 5 M^{-1} sec^{-1}, in good agreement with the observed value of 2.18 M^{-1} sec^{-1}. It thus appears that hydroxide ion is acting as a general base catalyst in the reaction with Malachite Green.

The reaction of tri-p-anisylmethyl cation with water was studied by Hill,[6] who concluded, on the basis of solvent isotope effects, that the reaction is not subject to general base catalysis. Hill found an equilibrium solvent isotope effect, K_{H_2O}/K_{D_2O}, of 2.7, and a kinetic solvent isotope effect of 1.2. We previously reported a kinetic solvent isotope effect of unity for the reaction of Crystal Violet cation with water. The reverse reactions, formation of carbonium ion from alcohol, must then have a kinetic solvent isotope effect of ca. 0.44 (i.e. 1.2/2.7), which is in the range commonly associated with specific acid catalysis.[7] The present results, of course, show that these reactions involve general acid catalysis.

The situation appears to be quite similar to that encountered in the hydrolysis of ortho esters where solvent isotope effects indicated specific acid catalysis (i.e. k_{H_2O}/k_{D_2O} ranges from 0.4 to 0.7) while more recent results clearly indicate general acid catalysis.[8] It is also worth noting that recent studies have shown that the hydrolyses of some acetals and ketals involve general acid catalysis.[9]

The implications of the present results on the interpretation of experiments involving the trapping of carbonium ions in solvolysis reactions[10] are obvious and are the subject of work underway in our laboratories.

(6) E. A. Hill and W. J. Mueller, Tetrahedron Lett., 2565 (1968).
(7) P. M. Laughton and R. E. Robertson in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 7.
(8) E. H. Cordes, Progr. Phys. Org. Chem., 4, 1 (1967).
(9) T. H. Fife and L. H. Brod, J. Amer. Chem. Soc., 92, 1681 (1970).
(10) C. D. Ritchie, ibid., 93, 7324 (1971).

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Introduction of a 9(11) Double Bond into Steroids by Selective Free-Radical Halogenation

Sir:

In the course of our studies[1] on remote oxidation, involving the functionalization of steroids by the use of oriented reagents, we came across indications[2] that certain simple free-radical halogenations with selective reagents could also be used to achieve the synthetically important introduction of a 9(11) double bond into steroids. Unsaturation at 9(11) provides an entry into the medicinally useful corticosteroid series.

(1) (a) R. Breslow and M. A. Winnik, J. Amer. Chem. Soc., 91, 3083 (1969); (b) R. Breslow and S. W. Baldwin, ibid., 92, 732 (1970); (c) R. Breslow and P. C. Scholl, ibid., 93, 2331 (1971); (d) R. Breslow and P. Kalicky, ibid., 93, 3540 (1971).
(2) Cf. Ph.D. Thesis, W. N. Washburn, Columbia University, 1971. Some of these observations have been described in public lectures as early as June 1970.