The Effect of Pressure on the Rate of Alkaline Fading of Malachite Green. A Reinvestigation

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Abstract: The rate of aqueous alkaline fading of Malachite Green (tetrafluoroborate salt) has been determined at 25 °C over a range of pressures and pH values. This net anion–cation combination reaction is confirmed to be subject to general base catalysis; both a water and hydroxide ion pathway contribute. The water reaction is accelerated by pressure; the activation volume equals -12 ± 1 cm^3/mol. The hydroxide ion pathway is independent of pressure when observed with a Dabco buffer. The first ionization volume of Dabco was determined; when this is taken into account, the ion recombination reaction is found to have a normal, positive volume of activation of $+15$ cm^3/mol. The overall effect of pressure on the reaction, first observed by Laidler, is thus explained. The reaction volume was determined in methanol and also found to be positive; thus, the entire reaction profile can be drawn. Direct measurements of the partial molar volumes of quinone and *p*-dimethoxybenzene do not reveal the unusually large space requirements by the former that have been postulated in the literature.

Introduction

In the preceding paper,[1] it was pointed out that of the several thousand measurements of reaction and activation volumes recorded to date, there are but a handful that cannot be adequately explained in terms of reasonable mechanisms. These exceptional cases are of obvious interest, in that they hold out the promise either of revealing new insights should the reported data be correct, or of allowing corrections to be made to the literature should it be found to be faulty in this respect; in either case, such exceptions once felt to justify doubts about our understanding can become the principal support of it once their true nature has been grasped.

Possibly the most puzzling of these exceptional cases has been that of the alkaline fading of certain triphenylmethane dyes under pressure. In 1959, Chen and Laidler reported[2] that the fading of Malachite Green in aqueous base at 25 °C and over a range of more than 100 MPa (1 MPa ≈ 10 atm) has a volume of activation of −12.0 cm^3/mol. This result makes that reaction the only one to have been observed before or since that features a pressure-enhanced neutralization of ions. All of the hundreds of acid–base and ion-pair equilibria and all of the solvolytic displacement reactions, trans-acylations, and even ionogenic fragmentation reactions known to date are affected by pressure so as to promote the appearance and inhibit the disappearance of ionic charge. The now obvious reason for this very general phenomenon is simply that the solvation of ions is characterized by a large volume reduction (electrostriction),[3] resulting from the polarization, orientation, attraction, and hence compression of solvent molecules by the powerful local fields of the ions. Laidler concluded from his astounding results that in the ionic triphenylmethane dyes, the quinoidal structural feature must have an unusually large volume, and that the loss of this quinoidal character in the reaction must be more important that the loss of electrostriction. He supported his argument with the supposition that the delocalization of charge to the nitrogen atoms must reduce the initial electrostriction. While this is true, it ignores the exceedingly strong solvation of hydroxide ion (which has a *negative* partial volume[4]). Nor does it explain why the quinoid group, along among virtually all other organic functional groups, should require a special correction in its parachor.[5]

Results and Discussion

Laidler's explanation—which continues to be quoted and applied[6]—is open to a simple and direct test. The partial volumes of the model compounds *p*-quinone and *p*-dimethoxybenzene were calculated from densities of solutions in acetonitrile, determined as a function of concentration. The usual extrapolation to infinite dilution gave as the results 112.0 and 147.6 cm^3/mol, respectively, so that the difference for these two compounds, differing by the elements of ethane, equals 35.6 cm^3/mol (see also Figure 4 below). If one considers that the increment in molar volume along homologous series is generally about 16–17 cm^3/mol of *methylene*, the difference we observe is not revealing an unusually large size as characteristic of the quinoid structure. As a further test, we then decided to measure the reaction volume for the neutralization of Malachite Green. The idea was that if some structural feature such as that advanced by Laidler could dominate the volume change in the transition state, then it surely would do so at least as much or even more in the final state; i.e., ΔV should also be negative, and probably more so that $\Delta V^{\ddagger}$.

Reaction volumes can be obtained in several ways:[7] by the proper combination of the partial molar volumes of all the participating species in the stoichiometric equation, from the effect of pressure on the overall equilibrium constant, and by means of dilatometry. None of these methods is completely satisfactory in the present case. The low solubility of the carbinol in water rules out the first approach. The second can in pinciple be done; however, it would have to be at a lower pH than that used by Laidler if the dye concentration is to be measured spectroscopically, and one should then have to worry about N-protonation and other caveats. The third approach again requires concentrations well above the solubilities. In order to make progress, we decided to do the dilatomeric measurement, but in methanol; in this solvent the solubilities were found to be adequate, and the availability of at least a few ionization volume data in both water and methanol would presumably allow us to make a crude extrapolation to water should the need arise. The fact that the reaction of Malachite Green with methoxide ion is bimolecular and very fast necessitated the use of a special dilatometer, described in Figure 1 and in the Experimental Section. It allowed the complete filling of the reservoir with the separate solutions, mixing them at a time of choice, and measuring the corrections required by dilution effects and the heat of reaction.

The result of these measurements is that the reaction volume for the formation of the methyl ether is +20.8 cm^3/mol. This value would be reduced if water could be used (see below), but there is no possibility that the sign would change. Thus, this result deepens the suspicion that there is something wrong with Laidler's data or interpretation.[8,9]

(1) W. J. le Noble, K. R. Brower, C. Brower, and S. Chang, preceding paper in this issue. The present article was also presented as part of a plenary lecture at the Eighth Airapt Conference in Uppsala, Sweden, 1981.
(2) D. T. Y. Chen and K. J. Laidler, *Can. J. Chem.*, **37**, 599 (1959).
(3) P. Drude and W. Nernst, *Z. Phys. Chem. (Leipzig)*, **15**, 79 (1894).
(4) F. J. Millero, *Chem. Rev.*, **71**, 147 (1971).
(5) Q. R. Quayle, *Chem. Rev.*, **53**, 439 (1953). The parachor of an atom or group is its contribution to the molar volume at a standard surface tension.

(6) For a recent example, see H. Maruno, T. Okubo, and N. Ise, *Ber. Bunseges. Phys. Chem.*, **85**, 667 (1981).
(7) W. J. le Noble, *Rev. Phys. Soc. Jpn.*, **50**, 207 (1980).
(8) The rather modest magnitude of this value can be ascribed to the delocalized charge in the cation (ref 3).

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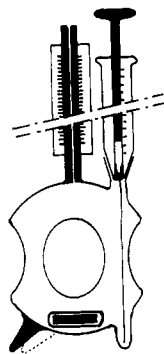
Figure 1. A dilatometer usable for fast, bimolecular reactions. A clamp used to hold the plunger rigidly in place has been omitted.
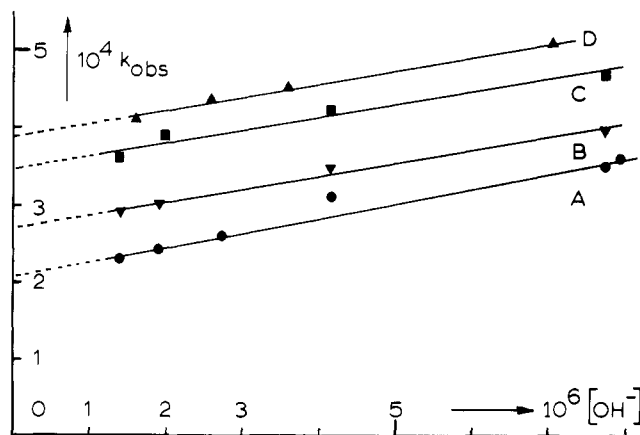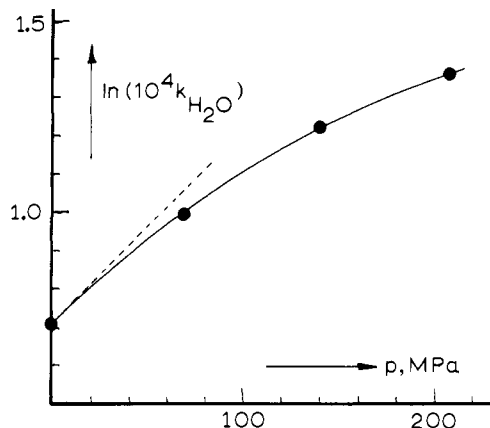

Figure 2. The effect of pH on the fading of Malachite Green at various pressures. A, B, C, and D represent pressures of 0.1, 69, 139, and 208 MPa, respectively. The 1-atm line virtually coincides with Ritchie's data.

The key to this riddle is Ritchie's observation that some cation–anion reactions, the alkaline fading of Malachite Green among them, are subject to general-base catalysis.[10] Thus, even though the stoichiometry shows only hydroxide as reacting with Malachite Green, in fact, neutral water is also competing for this cation, giving protonated trityl carbinol which subsequently neutralizes the base. This is obvious from Ritchie's determination of the pH dependence of the observed rate constant; the finite intercept at zero base concentration leaves no doubt about this. Since Laidler's measurement was done at one pH value, the pressure effect he observed is a composite of the effects of two reaction pathways leading to the same products. After the appearance of Ritchie's papers, it seemed likely that the water reaction had made a major (approximately 50%) contribution in the study of Chen and Laidler. Furthermore, since this pathway is likely to be pressure-accelerated as one involving bonding without loss of charge, it should become even more important at high pressure if the hydroxide reaction is indeed suppressed then as suspected all along. The experiment required is conceptually simple: one needs to remeasure Ritchie's plot, but now as a function of pressure so as to yield the pressure coefficients of both reactions.

In practice, this turns out not to be simple. In order to keep the extrapolations to zero hydroxide concentration reasonably

Figure 3. Effect of pressure on the water-mediated fading of Malachite Green, and the slope at zero pressure.

short, the rate constants must be measured in buffered solutions whose pH values are themselves pressure dependent. Unusually high precision in the rate observations is necessary in order to calculate the separate rate constants and thence the activation volumes to any degree of reliability.

The raw results, uncorrected for the pressure-induced pH changes, are shown in Figure 2. Our data at atmospheric pressure agree well with Ritchie's. It is clear that the overall rates are increasing with pressure, as reported by Chen and Laidler.

The effect of pressure on the value of k_{H_2O} (the intercept at zero hydroxide ion concentration) is shown in Figure 3. The slope at zero pressure equals $-\Delta V^{\ddagger}/RT$, and the activation volume for the water reaction thus calculated equals -(12 ± 1) cm^3/mol. This negative value is about what would normally be expected for a reaction characterized by the formation of a new bond and by the localization of the initially dispersed charge.[11]

The fact that this result is exactly the same as the Chen–Laidler value requires comment. Ritchie showed that in Laidler's atmospheric pressure experiment, the contribution by hydroxide ion must have been about 50%, and if this contribution is diminished by pressure (see below), Laidler's slope should have been less than ours; furthermore, their curve should have been S-shaped as the water contribution rises with the pressure. Thus, the fact -12 cm^3/mol is given in both reports is not indicative of agreement.

In principle it should be possible to correct Figure 2 completely for the effect of pressure on the pH. What is needed for this is the effect of pressure on K_w, which is known,[12] and that on the ionization constant of the base used (Dabco[13]), which is not. Since the information we now seek is the activation volume of the hydroxide reaction at atmospheric pressure, we have elected to be content with correcting the apparent activation volume of the hydroxide reaction by means of the ionization volume at atmospheric pressure of Dabco alone, since this base is the principal source of hydroxide. This procedure discards the possibility of extracting additional information such as the compressibility of activation for this reaction, but this is at best of marginal interest.

As can be seen in Figure 2, the slopes are equal in our pressure range to within experimental error, and hence the apparent activation volume $\Delta V^{\ddagger}_{OH^-}$ equals zero. In order to correct this value for the pressure effect on pH, we need to appraise the volume change for hydroxide ion by the process

$$Dabco + H_2O \rightarrow DabcoH^+ + OH^-$$
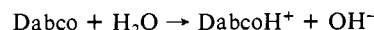
The volume change for this reaction can be assessed from

$$\Delta V_i = \bar{V}_{Dabco \cdot HCl} + \bar{V}_{NaOH} - \bar{V}_{Dabco} - \bar{V}_{NaCl} - V_{H_2O}$$

(9) We became aware after the completion of our work that N. S. Isaacs had also subjected Laidler's conclusion to this test, and had qualitatively obtained the same result. He, too, points out the major discord represented by this reaction: "Liquid Phase High Pressure Chemistry", Wiley, New York, 1981, p. 237. We are indebted to Professor Isaacs for a copy of his book.

(10) (a) C. D. Ritchie, D. J. Wright, D. S. Huang, and A. A. Kamego, *J. Am. Chem. Soc.*, **97**, 1163 (1975). This work is the culmination of contributions by several groups: (b) R. A. Diffenbach, K. Sano, and R. W. Taft, *J. Am. Chem. Soc.*, **88**, 4747 (1966); (c) J. W. Bunting and W. G. Meathrel, *Can. J. Chem.*, **51**, 1965 (1973); **52**, 951, 962, 975, 981 (1974); (d) C. A. Bunton and S. K. Huang, *J. Am. Chem. Soc.*, **94**, 3536 (1972); **95**, 2701 (1973); **96**, 515 (1974); (e) J. H. Ride, P. A. H. Wyatt, and Z. M. Zochowski, *J. Chem. Soc., Perkin Trans.* **2**, 1188 (1974). See also: (f) C. D. Ritchie, G. A. Skinner, and V. G. Badding, *J. Am. Chem. Soc.*, **89**, 2063 (1967).

(11) W. J. le Noble, *Prog. Phys. Org. Chem.*, **5**, 207 (1967).

(12) F. J. Millero, E. V. Hoff, and L. Cahn, *J. Solution Chem.*, **1**, 309 (1972).

(13) The pK_a of Dabco is only known at atmospheric pressure (8.8 at 25 °C in water): P. Paoletti, J. H. Stern, and A Vacca, *J. Phys. Chem.*, **69**, 3759 (1965).
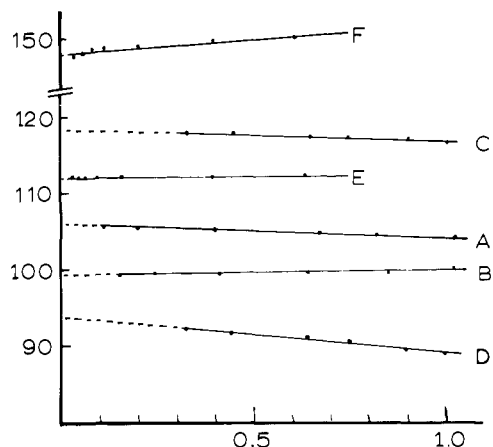
Figure 4. Apparent molal volumes of Dabco in water (A) and in methanol (B), the hydrochloride in water (C) and in methanol (D), and of quinone (E) and p-dimethoxybenzene (F) in acetonitrile at 25 °C. The horizontal scale is C for the neutral compounds and $\sqrt{C}$ for the salt; the vertical scale is ϕ_V for the neutral compounds, ϕ_V −1.868$\sqrt{C}$ for set C and ϕ_V −15.77$\sqrt{C}$ for set D. The extrapolation to infinite dilution was done by least-squares fitting.

The partial volumes of the amine and its hydrochloride were evaluated in duplicate experiments by extrapolation of the apparent molar volume (caculated from densities) to infinite dilution. We have described our basic methods before;[14] the only change is that we now use a tuning fork densimeter instead of pycnometers. The precision of the result can be gauged from Figure 4. The ionization volume is therefore ΔV_i = 117.8 + (−6.8) − 106.0 − 16.6 − 18.0 = −29.6 cm^3/mol. This is quite close to the values of other amines.[15]

Applying $\partial \ln K/\partial p = -\Delta V_i/RT$, we thus find that K_B begins to increase by a factor of 3.2 per kbar as the pressure is raised from atmospheric, and hence the hydroxide ion concentration begins to increase by a factor of 1.8 (or 3.2$^{1/2}$) per kbar. One could similarly multiply all hydroxide concentrations by the factor appropriate for the pressure used. The correction is thus obviously half of the ionization volume; in other words, $\Delta V^*_{OH^-}$ = +15 cm^3/mol. Clearly, the insensitivity of the hydroxide ion catalyzed reaction is only apparent. We note in passing that our results with Malachite Green resemble those obtained by Virtanen[16] for the dissociation of decavanadate anion in water; in this instance, a positive value was obtained for the neutral reaction, and a negative activation volume for the hydroxide ion catalyzed branch.

The data now available permit the construction of the volume profile (see Figure 5). The volume scale in this figure is given in cm^3/mol, but it is not absolute since we cannot determine the partial volumes of either the dye or the product alcohol in water. The reaction volume of +14.2 cm^3/mol is an estimate based on a comparison of the absolute values of the ionization volumes of anions in water and in methanol, the latter generally being about 50% larger than the former.[15]

The figure suggests that the reverse of the water reaction:

$$ROH + H_2O \rightarrow ROH_2^+ + OH^-$$
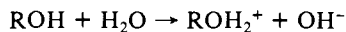
would have an activation volume of −26 cm^3/mol. This value is similar to the volume change for the autoionization of water,[12] which gives one confidence in the internal consistency of our data. The slight volume maximum displayed in the figure for the hydroxide reaction is unexpected. It is possible, of course, that this superficially simple reaction is more complex than the stoichiomatric equation suggests; thus, the initial neutralization
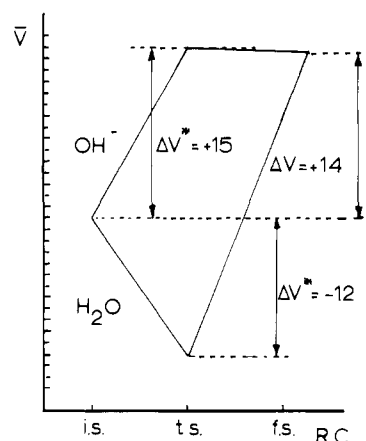
product may be an ipso alcohol which then rearranges in rapid steps. One is reminded of the surprise finding by Nauta and MacLean that the trityl radical dimer was not hexaphenylethane, but a product resulting from the involvement of one of the para carbon atoms.[17] However, the multitude of experiments going into the construction of Figure 5 is perhaps too great to warrant attaching much significance to the maximum.

We conclude as follows. The net results agree with all other experience in high-pressure chemistry: bond formation (as in the water reaction) leads to a volume decrease and therefore rate enhancement by pressure; neutralization (as in the hydroxide process) leads to desolvation, volume expansion, and a decreased rate under pressure. Contrary to the earlier impression, the fading of Malachite Gree is unexceptional in these respects.

Experimental Section

Materials. p-Quinone and p-dimethoxybenzene were recrystallized several times before use. Malachite Green (from Aldrich) was converted from the chloride salt into the tetrafluoroborate as described;[18] the product was crystallized twice from water (at pH 4) and dried under vacuum before use. Dabco was crystallized from heptane and then sublimed. Samples used for density determinations were resublimed before use and stored under vacuum over Drierite. The hydrochloride salt was prepared by the addition of calculated amount of hydrochloric acid in ether to a cold solution of Dabco in either. The precipitate was filtered under exclusion of moisture, crystallized from anhydrous methanol–ether, dried in a drying pistol, and stored under vacuum over phosphorus pentoxide. Solutions of potassium hydroxide, hydrochloric acid, and perchloric acid were standardized by use of potassium acid phthalate.

Measurements. Solution densities were measured by means of a densimeter (Sodev Inc., Model 02-D) equipped with a programmable circulating thermostat (Model CT-C), and a Newport coutertimer (Model 700) and digital printer (Model 810). Calibration was done with water and with methanol, the densities for which are known to ±0.00002 g/cm^3; checks were made with heptane, acetone, carbon tetrachloride, and sodium chloride solutions.[19] The densities of solutions of Dabco and its hydrochloride in water and in methanol were used to calculate the partial molar volumes:

$$\phi_V = \frac{M}{d_0} - \frac{\Delta d}{d_0}\frac{1000}{C}$$

These volumes were then extrapolated to infinite dilution.

The reaction volume for the reaction of Malachite Green tetrafluoroborate was measured by means of the dilatomer shown in Figure 1, especially designed for fast, bimolecular reactions. The diameter and

Figure 5. The volume profiles of the reactions of Malachite Green with hydroxide ion and with water 25 °C. The divisions and volume changes are in cm^3 mol.

(14) W. J. le Noble and T. Asano, *J. Org. Chem.*, **40**, 1179 (1975).

(15) See, for example, S. D. Hamann, *Mod. Aspects Electrochem.*, **9**, 47 (1974). We also determined ΔV_i in methanol at 25 °C; the result is −46.0 cm^3/mol. Thus, in this solvent also, Dabco resembles simple trialkylatmines: H. Inoue, K. Hara, and J. Osugi, *Rev. Phys. Chem. Jpn.*, **48**, 44 (1978).

(16) P. O. I. Virtanen, M. Puutio, and T. Kuokkanen, *Finn. Chem. Lett.*, 135 (1980).

(17) H. Lankamp, W. T. Nauta, and C. MacLean, *Tetrahedron Lett.*, 249 (1968).

(18) C. D. Ritchie, W. F. Sager, and E. S. Lewis, *J. Am. Chem. Soc.*, **84**, 2349 (1962).

(19) P. Picker, E. Tremblay, and C. Jolicoeur, *J. Solution Chem.*, **3**, 377 (1974); see also, API 44-TRC, Selected Data on Thermodynamics and Spectroscopy, Thermodynamics Research Center, Texas A&M University, College Station, texas.

uniformity of the capillary bore were determined by measurement of the length of mercury columns and weighing the mercury; the diameter was found to be 1.005 mm. The flask is initially filled through the open joint with the methanolic dye solution (0.006 M); the 0.5-mL syringe, which had been ground to fit the joint, was filled with lithium methoxide in methanol (1.4 M; lithium was chosen because of the relatively high solubility of its perchlorate in methanol). The insertion must be done with care so that the needle is in the protuberance of the flask and such that no air bubbles are trapped. The methanolic dye solution rises somewhat into the capillary while this is done. Some epoxy adhesive is applied to the joint, since otherwise evaporation through the annular space between flask and syringe is a significant problem. The assembly is then thermostated, and the 0.5-mL syringe is emptied very slowly (during about 1 min), so that no significant mixing occurs. Then the level is adjusted to a desired level by means of another hypodermic syringe and read by means of suitable magnification. The magnetic stirrer is activated and left on for ~0.5 min, causing complete decolorization of the solution. The level undergoes a rapid rise during this time and then slowly falls again as the heat liberated by the reaction is liberated. It eventually (after 10–15 min) declines to a very slow constant rate caused by evaporation. Extrapolation of this very slow decline back to the time of mixing gives the corrected final reading. In order to do the experiment in a reasonably short time, the lithium methoxide was somewhat in excess. The dilution of the base produced a volume decrease which was evaluated independently. A correction for this effect was made; the calculation, too obvious to require recording here, shows that the reaction volume could be determined in this way with a reproducibility less than 1 cm³/mol.

The kinetics were followed at 25.00 ± 0.05 °C by means of a Cary 14 in an Aminco high-pressure optical cell with quartz windows, fitted with a cylindrical quartz sample cell, with mercury providing the flexible separation between hydraulic fluid (water–glycerin, 1:1 v/v) and reaction solution.[20] The pH of the solutions was measured by means of a Beckman research pH meter and a Duramark "pencil" combination electrode (Markson Scientific); this equipment was calibrated with standard buffers to ±0.001 pH unit.

The Dabco–perchlorate buffer was prepared according to a standard procedure.[21] The buffer base concentration was 2.0 × 10⁻³ M in all runs, and the ionic strength was maintained at 8.4 × 10⁻³ M by the addition of $KClO_4$ to the solutions. A 4 × 10⁻⁴ M master solution of Malachite Green tetrafluoroborate was prepared in anhydrous methanol containing a small amount of hydrochloric acid. A 1-mL portion of this solution was added to 9 mL of buffer and the kinetics were followed at 610 nm. All the reactions were followed for a minimum of 6 half-lives; the end absorbance was read after 12 half-lives. The pH of the reaction mixture was measured at regular intervals and found to be constant within ±0.01 pH unit. Pseudo-first-order rate constants were calculated from the slope of the plot ln $(A_t - A_\infty)$ vs. time, where A_t is the absorbance at time t and A_∞ is the end absorbance. All the data were subjected to least-squares fits.

Registry No. Malachite Green tetrafluoroborate salt, 60885-33-8; Dabco, 280-57-9; DabcoHCl, 2099-72-1; p-quinone, 106-51-4; p-dimethoxybenzene, 150-78-7.

(20) W. J. le Noble and A. R. Das, J. Phys. Chem., 74, 3429 (1970).
(21) R. g. Bates, "Determination of pH: Theory and Practice", Wiley, New York, 1964.

Temperature and Substituent Effects on Regioselectivity in the Insertion of Arylcarbene into Alcohols[1]

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Abstract: Photolysis of aryldiazomethanes in methanol, ethanol, and 2-propanol gave OH insertion products along with small amounts of CH insertion products at ambient temperature. However, the CH insertion products increased significantly at the expense of the ether as the temperature was lowered. The attempted sensitized decomposition of the diazomethane did not lead to an increase in the CH insertion products presumably because of a rapid singlet–triplet equilibrium. The key intermediate leading to the CH insertion is suggested to be ground-state triplet arylcarbene, based on the accumulated spectroscopic as well as chemical evidence for the intervention of the triplet arylcarbene in the low-temperature photolysis of aryldiazomethanes. Substituents on the phenyl ring also have an appreciable effect on the insertion selectivity. At room temperature, the OH/CH insertion selectivity increased with the electron-donating ability of the substituents. This is interpreted in terms of the substituent effect on the transition state of OH insertion, where there is a deficiency of electrons at the benzylic carbon atom, rather than on the stability of singlet carbene. At low temperature, both electron-donating and -withdrawing substituents facilitate OH insertion, indicating that the change in substituents induces a concomitant change in the insertion mechanism, presumably due to decreasing nucleophilicity of carbene with increasing electron-withdrawing ability as well as decreasing proton–donor activity of alcohol with decreasing temperature. This may also reflect the effect of the substituent on the singlet–triplet energy gap.

Carbene chemistry is of interest to both mechanistic and synthetic organic chemists especially on the subject of spin states and intrinsic reactivity. Although the current era of carbene chemistry began with the recognition of the two characteristic carbene reactions, insertion into C–H bonds and addition to C–C double bonds, the most widely used diagnostic for spin state has been the latter reaction.[2] This is because of a stereochemical label to distinguish between the concerted (singlet) and stepwise (triplet) nature of the addition reaction. A mechanistic ambiguity on the exact multiplicity responsible for CH insertion was recognized since abstraction of a hydrogen atom followed by coupling of the radical pair could give rise to the same products as concerted

(1) (a) Carbene in Rigid Matrix. Part XII. (b) For a preliminary description of the present work, see: Tomioka, H.; Izawa, Y. J. Am. Chem. Soc. **1977**, 99, 6128.

(2) See, for reviews: (a) Kirmse, W. "Carbene Chemistry", 2nd ed.; Cademic Press: New York, 1971. (b) Moss, R. A., Jones, M., Eds. "Carbenes"; Wiley: New York, 1973, 1975; Vol. I, II.