Volume Profiles for Reactions of Malachite Green with Anionic Nucleophiles

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Volumes of activation and volumes of reaction for the reaction Malachite Green$^+$ + Y$^-$ ⟶ Malachite Green-Y have been measured for six different Y$^-$ in eight different solvents. The volumes of activation are negative (-4 to -20 cm^3 mol^{-1}) whereas volumes of reaction are positive ($+10$ to $+30$ cm^3 mol^{-1}) which is expected for a reaction involving charge neutralisation. In these solvents, contributions to the volumes of activation from reaction of neutral solvent are absent and the explanation of the negative values is sought in two possible models. Either, the reaction requires an initial anion separation from its counterion with which it exists as a relatively unreactive ion-pair or, the activation process requires rehybridisation and charge concentration on the Malachite Green central carbon leading to an increase in electrostriction during activation.

Laidler and Chen, while investigating the effects of solvent electrostriction on volumes of activation, reported values for the alkaline fading of a number of cationic triphenylmethane dyes and against expectations found these without exception to be zero or substantially negative.[1,2]

The dyes examined included Crystal Violet, Malachite Green, Bromophenol Blue, and phenolphthalein and in all cases the basic reaction is the attachment of hydroxide ion to form the colourless carbinol. Scheme 2 applies to the reaction of Malachite Green. All the dye molecules are planar and the cationic charge is highly delocalised onto substituents on the aromatic rings. Nevertheless, it would be expected that the neutralisation of charge by the anion would result in a considerable increase in volume. Therefore, the volume of reaction should be positive, and, if one assumed that the transition state was somewhere intermediate in charge distribution between reagents and products, the volume of activation should be positive also.[3,4] This would be a result of the release of electrostricted solvent (water). The experimental results, however, point to some additional complexity in the reaction and the inadequacy of the simple anion–cation recombination model depicted above. Upon reflection this is not perhaps unexpected since the reactions are very slow compared to the diffusion-controlled rates which are often experienced for simple anion–cation reactions.[5] Recently, the reaction of Malachite Green with hydroxide ion in water has been subjected to scrutiny by LeNoble et al.[6] who determined the volumes of activation over a range of pH values. These workers separated contributions due to reaction with hydroxide ion and to neutral water and concluded that the volume of activation for attachment of OH$^-$ is $+15$ cm^3 mol^{-1} as expected for charge neutralisation but that due to water is -12, presumably due to binding of a water molecule without any loss of charge. This accounts for the activation volume observed by Chen and Laidler, -12 cm^3 mol^{-1}, as resulting in part from the water reaction and in part from the increase in the hydroxide ion concentration due to water auto-ionisation ($\Delta \bar{V}$ -24 cm^3 mol^{-1}) as the pressure is raised. The volume of reaction was determined from the sum of partial molar volumes of individual reagents and products measured in methanol and was found to be positive also, as expected. The reactions of these triphenylmethane dyes with a variety of anion–solvent combinations has been intensively studied by Ritchie and his co-workers[7–10] using these cations to derive the nucleophilicity parameter, N^+. The relative nucleophilicities of water and aqueous OH$^-$ are 1 : 30,000 so that it seems unlikely that, in the 0.2M-sodium hydroxide solution that Chen and Laidler used, there would be much contribution to
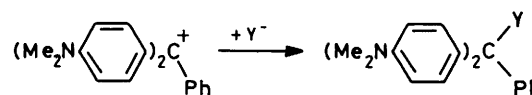
Scheme 1.

the rate from attack by water. We have therefore studied rates of reaction of Malachite Green with a variety of nucleophilic anions in solvents of widely different character with the aim of avoiding complications which may arise when a protic solvent and its lyate ion are the reagents. Systems were chosen in which rates were fairly slow (half-life at least 1 h). By adjustment of concentrations it was found that some reactions proceeded to equilibrium and equilibrium constants could be measured as a function of pressure. Thus, we were able to measure both volumes of activation and reaction for the same system in several cases. In others, only one or the other could be obtained by available techniques.

Experimental

Malachite Green tetrafluoroborate was prepared by dissolving technical grade Malachite Green (3.5 g) in hot water, filtering and adding a hot, saturated solution of sodium tetrafluoroborate (10 g). On cooling, dark green crystals formed which were filtered and dried *in vacuo* to constant extinction coefficient ($\varepsilon_{max.}$ 575 $\times$ 10^{-1} in ethyl acetate).

Tetra-alkylammonium Salts.—The following procedure was typical. Tetraethylammonium chloride (0.1 mol) and sodium nitrite (0.1 mol) were dissolved in hot ethanol and the solution allowed to stand on a steam-bath for 1 h. Part of the ethanol was removed on a rotary evaporator and benzene was added. The mixture was maintained at 50—60 °C until sodium chloride began to crystallise when it was set aside in the cold for complete precipitation to occur. After filtration, the solution was evaporated to dryness under vacuum and the crude tetraethylammonium nitrite recrystallised from ethyl acetate or acetone–ether. In a similar manner, the quaternary acetate, phenylsulphinate, and azide were prepared. Cyanide was used as the sodium salt.

Solvents.—In general, solvents were purified as recommended by Perrin et al.[11] Final purification in all cases was by fractional distillation, retaining a middle fraction.

Kinetic Procedure.—The following procedure was typical. A

Table 1. Rate constants for reaction between Malachite Green tetrafluoroborate and anions, Y^-

Solvent	$10^3[Y^-]/$ M	$T/°C$	p/bar	$10^3k_1/$ min^{-1}
Y^- nitrite				
Dimethyl sulphoxide	57.8	25	1	20.4
			450	26.1
			900	29.8
Acetonitrile	35.7	51	1	26.4
			600	34.9
			1 000	45.1
Nitromethane	30.8	30	1	27.0
			300	26.9
			600	35.8
2-Methoxyethanol	42.5	50	1	28.5
			400	26.7
			800	28.7
Methanol	2.11	26	1	39.8
			600	57.6
+5% H_2O	0.607	31	1	86.4
			600	103.7
			900	120
+10% H_2O	1.03	35	1	12.1
			450	15.5
			900	18.3
+17.5% H_2O	1.23	26	1	58.7
			450	68.5
			900	85.0
+20% H_2O	1.11	26	1	10.8
			450	15.0
			900	20.3
$Y^- =$ azide				
Methanol	7.28	25	1	23.9
			600	38.8
$Y^- =$ phenylsulphinate				
Dimethyl sulphoxide	5.34	43	1	48.6
			800	61.0
Methanol	1.33	22	1	30.0
			300	31.2
			600	33.6
$Y^- =$ acetate				
Dimethyl sulphoxide	0.117	23	1	56.8
			800	63.3
2-Methoxyethanol	1.60	38	1	44.5
			450	48.8
			900	55.9
Equilibrium constants				$10^{-3}K/l^{-1}$
Y = nitrite				
Methanol		24	1	24.1
			300	16.6
			600	11.3
			900	8.3
5% Aqueous methanol		26	1	5.94
			300	4.25
			600	2.90
			900	2.14
10% Aqueous methanol		35	1	2.12
			450	1.47
			900	1.08
17.5% Aqueous methanol		26	1	1.48
			300	1.08
			600	0.717
			900	0.490
20% Aqueous methanol		26	1	1.44
			300	1.06
			600	0.82
			900	0.63
30% Aqueous methanol		26	1	0.267
			280	0.202
			450	0.164
			900	0.106

Table 1 (*continued*)

Solvent	$10^3[Y^-]/$ M	$T/°C$	p/bar	$10^{-3}K/l^{-1}$
Dimethyl sulphoxide		25	1	237
			400	188
			800	154
2-Methoxyethanol		40	1	1.25
			400	1.01
			800	0.908
Acetone		29	1	1.39
			200	1.17
			400	0.98
			600	0.81
$Y^- =$ phenylsulphinate				
Ethyl acetate		22	9	1.29
			400	1.23
			800	1.16
$Y^- =$ azide				
2-Methoxyethanol		24	1	2.07
			400	1.45
			650	1.20
			900	1.02
$Y^- =$ acetate				
Methanol		21	1	12.0
			400	9.01
			800	7.19
$Y^- =$ phenylthiolate				
Methanol		26	1	524
			150	498
			300	466
			450	444
			600	411

* Standard errors are, on average, 1% for individual runs and 5% reproducibility.

solution of Malachite Green tetrafluoroborate (1 cm³; 2.5×10^{-5}M) in dimethyl sulphoxide was placed in a 10 cm³ volumetric flask and 7—8 cm³ of solvent added. The flask was brought to the thermostat temperature and the reaction initiated by addition of tetraethylammonium nitrite solution in dimethyl sulphoxide (1 cm³; 2×10^{-2}M). The mixture was transferred to the thermostatted cell (±0.1 °C) of a Beckman-25 spectrophotometer and the absorbance at the wavelength of maximum absorption (535 nm in this solvent) measured as a function of time. For high-pressure rate measurements, the solution was transferred to a sliding cell of the type described by LeNoble [12] and placed in a Nova Swiss high-pressure optical cell used in a Beckman-25 spectrophotometer. All runs were conducted in duplicate. Since the nucleophile is present in large excess, all rates were calculated as pseudo-first-order processes by the Guggenheim method [13] using a computed least-squares fit and converted to second-order rate constants. Equilibrium measurements were carried out in the high-pressure cell and after each change of pressure time allowed for the establishment of equilibrium by observing the change in absorbance. The use of the sliding cell permits absorbance changes to be measured without the need for correction due to solvent compression. Volumes of activation and volumes of reaction were calculated from rate and equilibrium constants, respectively, by the relationships $-RT\, \partial \ln k/\partial P = \Delta V^\ddagger$ and $-RT\, \partial \ln K/\partial P = \Delta V$.

Discussion

The results are summarised in Tables 1 and 2 from which it appears that volumes of reaction are all positive as expected for a chemical change involving charge neutralisation overall. The actual values of V are solvent-dependent which is to be

Table 2. Volumes of activation and volumes of reaction for reactions of Malachite Green with anions Y^-

Solvent	Y^-	$T/°C$	$\Delta V^{\ddagger}/cm^3$ mol^{-1}	$\Delta V/cm^3$ mol^{-1}
Dimethyl sulphoxide				
	Nitrite	30	-8	$+13$
		25		$+12.5$
	Azide	30		$+16$
	Phenyl-sulphinate	43	-6	
	Acetate	23	-4	
Methanol				
	Nitrite	24	-16	
		24		$+28$
	Azide	25	-20	$+18$
	Phenylthiolate	26	-7	$+12$
	Phenyl-sulphinate	22	-4	
		20		$+20$
	Acetate	22	0	
		21		$+15$
Aqueous methanol	5%	31	-8.4	
		26		$+28$
	10%	35	-8.3	$+18$
	17.5%	26	-11	$+30$
	20%	26	-16	$+25$
	30%			$+25$
Water	Hydroxide	24	-8.5	
2-Methoxyethanol				
	Nitrite	50	0	
		40		$+10$
	Azide	24		$+19$
	Phenyl-thiolate	43	-18	
	Acetate	38	-5.6	
Dimethyl-formamide				
	Nitrite	30		$+21$
	Azide	30		$+26$
Acetonitrile				
	Nitrite	51	-13.7	
	Azide	21		$+28$
Nitromethane				
	Nitrite	30	-12	
	Azide	22		$+20$
Rearrangements, nitrite		nitro		
Ethyl acetate		25	-15	$+37$
Acetone		25	-6	$+9$

* Standard errors are ± 1 cm^3 mol^{-1}.

expected since they result almost entirely from differences in solvation of reagents and products. By contrast, volumes of activation are uniformly negative with reaction rates accelerated by pressure in all solvent–nucleophile systems studied. This unusual feature, a change in sign of the volume change in activation and post-activation stages of the reaction is apparently general and not confined to lyate ion attack, albeit that the explanation for the water system may well be correct or at least a part of the correct interpretation. We have considered two models for this behaviour.

Ion-pair Effects.—From conductivity data for quaternary ammonium salts in our solvent systems [14] it seems probable that the anionic reagents are significantly ion-paired. For example, the association of tetraethylammonium iodide shows the following solvent dependence: [15]

$$Et_4N^+ + I^- \rightleftharpoons (Et_4N^+I^-); \quad K_a = \frac{(X^+Y^-)}{(X^+)(Y^-)}; \quad K_d = 1/K_a$$
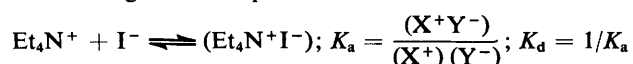
Solvent	$10^{-3}K_d/l\ mol^{-1}$
Acetone	7.93
Acetonitrile	90.9
Butan-1-ol	0.714
Dimethylformamide	73
Ethanol	7.5
Methanol	52.6

It is possible that the reactivity of free anion is far greater than that of the ion-pair [16] so that reactions (1) and (2) apply whence $\Delta V^{\ddagger}_{exp} = \Delta V_d + \Delta V^{\ddagger}$. Volumes of dissociation of ion-pairs are inevitably negative due to the increase in

$$(X^+Y^-) \xrightleftharpoons{K_d} X^+ + Y^- \quad \Delta V_d \qquad (1)$$

$$R^+ + Y^- \xrightarrow{k} R\text{-}Y \quad \Delta V^{\ddagger} \qquad (2)$$
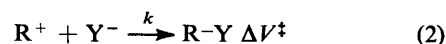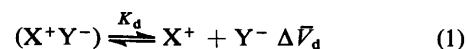
electrostriction in converting a dipole into two ions.[17,18] For tetramethylammonium bromide in propan-2-ol, $\Delta V_d = -21$cm^3 mol^{-1},[18] but such values are very solvent-dependent being more negative in solvents of low polarity and conversely. A large, negative value of ΔV_d in conjunction with a smaller positive $\Delta V^{\ddagger}$ due to partial charge neutralisation could account for the observed experimental values of $\Delta V^{\ddagger}_{exp}$. The latter would be dominated by ΔV_d and hence would be expected to be more negative in solvents of low polarity whereas the opposite is the case. The observed activation volumes for reactions of nitrite become more negative in the solvent order 2-methoxyethanol, dimethyl sulphoxide, methanol, acetonitrile, and more negative with increasing water in aqueous methanol. A second model may be considered.

If ion-pairing is irrelevant, *i.e.* either the reactivities of free ion and ion-pair are sufficiently similar or that reaction takes place entirely by attack of ion-pair whatever the pressure, then we need a model which accounts for an increase in the solvation of the reactants during the activation process. The Malachite Green cation is large and bears a highly diffuse charge, mainly located on the amino-groups. This would be associated with weak solvation. We envisage the approach of the nucleophile as bringing about a change in hybridisation leading to a solvent-separated ion-pair, in which the cationic charge is highly concentrated. This may be considered a reactive intermediate but would plausibly be more highly solvated than the free Malachite Green cation giving rise to the observed negative volume of activation. In this case it is difficult to predict the solvent effect upon the value of $\Delta V^{\ddagger}$ since the location of the transition state may alter with a change of medium. At present it seems difficult to distinguish the merits of either model without further information but the results serve to point up the presence of complexities in mechanism, probably bound up with solvent properties, in an apparently simple reaction. One further point was observed. Reactions of Malachite Green with nitrite in acetone and in ethyl acetate proceeded rapidly to equilibrium, too rapidly for rate measurements to be made. Subsequently a slow reaction was observed which proceeded to complete disappearance of the green colour. We believe this to be due to a rearrangement of the initially formed nitrite ester to the more stable nitro compound (Scheme 3), an example of kinetic and thermodynamic control on product formation. Volumes of activation for this rearrangement are negative which is to be expected since both steps, the dissociation of the nitrite and the subsequent attachment of the nitrite ion at the nitrogen centre, will have negative contributions.

Scheme 2.

$$Ar_3C^+ + ONO^- \underset{slow}{\overset{fast}{\rightleftharpoons}} Ar_3C\text{-}ONO$$
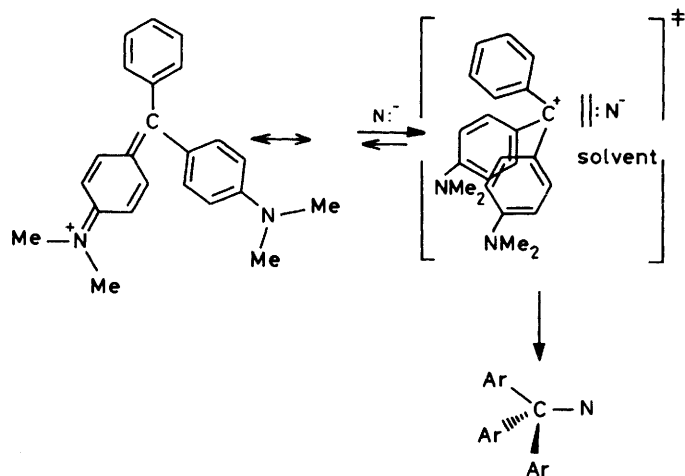
$$Ar_3C\text{-}NO_2$$
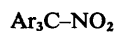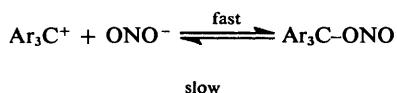
Scheme 3.

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