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THE k_{Br}/k_{Cl} ELEMENT EFFECT FOR NUCLEOPHILIC VINYLIC SUBSTITUTION OF THE HIGHLY REACTIVE TRICYANOVINYL-X SYSTEM BY SUBSTITUTED ANILINES[1]

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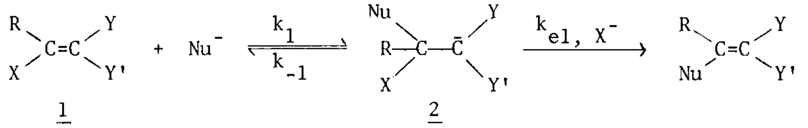
Abstract: *The element effects for the substitution of tricyanovinyl chloride and bromide by the p-position of three dialkylanilines are* $k_{Br}/k_{Cl}=2.37\pm0.18$. *An early transition state for the expulsion of the halide ion from the intermediate zwitterion is indicated.*

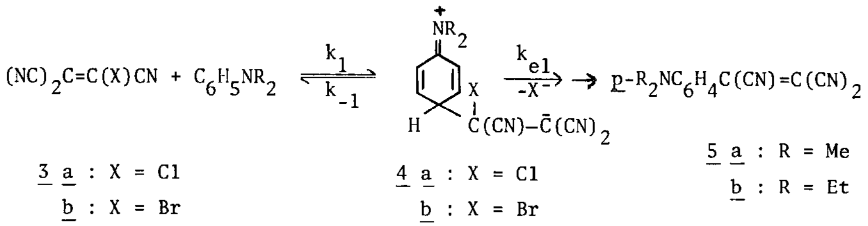
According to the theory of the variable transition state of nucleophilic vinylic substitution[2] the substitution of 1 by the nucleophile Nu^- (eq. 1) is a multi-step process involving the carbanion 2 when the activating groups Y and Y' are highly capable of delocalizing a negative charge. A tool used extensively for supporting this route is the k_{Br}/k_{Cl} "element effect" when the nucleofuge X is an halogen.[2,3] The observed k_{Br}/k_{Cl} values of around unity and the relatively high k_F/k_{Cl} values are mostly interpreted as reflecting a rate determining nucleophilic attack (k_1), for which the order Br ∾ Cl << F is expected. A different order (Br > Cl >> F) is predicted for a rate determining k_{el}. However, a k_{Br}/k_{Cl} value of ∾1 is not unequivocal evidence for a multi-step route. It may also be ascribed to a concerted single-step substitution with 2 as a transition state involving only a slight C-X bond elongation (i.e., an uncoupled concerted reaction).[4]



(1)

These alternatives may be distinguished by studying the element effect for a sufficiently highly activated system known to react via a step-wise process. The observation of amine catalysis for 1,Y=Y'=CN[5] or of stereoconvergence when Y=CN, Y'=CO_2Me[6] indicates the operation of the multi-step process. Systems activated by these groups give k_{Br}/k_{Cl} ratios close to unity and similar to those for less activated systems.[2,3,7] It is therefore of interest to inquire whether the use of even more activated systems, where nucleofuge expulsion is presumably involved in the rate determining step, will increase the k_{Br}/k_{Cl} ratio above its value for the less activated systems.

We chose for our study the reaction of tricyanovinyl-X system 3 with substituted anilines (eq. 2) for three reasons. First, the negative charge dispersal ability of the system is higher than of any other system studied previously: based on the pKa's of anilinium ions[8] $\sigma_I = 0.60$ and $\sigma_R = 1.08$ for $C(CN)=C(CN)_2$, compared with $\sigma_I = 0.55$, $\sigma_R = 0.61$ for NO_2. Second, this is the most activated vinylic system studied kinetically so far. Third, the second order substitution



(2)

of tricyanovinyl chloride 3a with N,N-dialkylanilines[9] gives the p-substitution products 5[10] in a process having very low activation energies (1.4 - 2.6 kcal mol^{-1} for R=Me, Et, Pr, Bu). The intermediates are the zwitterions 4, from which nucleofuge expulsion would be slower than from a carbanion and indeed it was suggested that $k_{-1} >> k_{el}$ so that the observed rate constant is composite, i.e., $k_{obs} = k_1k_{el}/k_{-1}$. Hence, system 3 is a most promising candidate for estimating the element effect on k_{el} via the measured effect on k_{obs}.

Tricyanovinyl bromide (3b) is unknown. We prepared it several times by a procedure analogous to the preparation of tricyanovinyl chloride (3a).[10] Oxalyl bromide was added to a cold stirred suspension of tetramethylammonium tricyanoethenolate $(NC)_2C=C(CN)\bar{O}\overset{+}{N}Me_4$ in dry ether-dimethoxyethane under nitrogen, the mixture was stirred for an additional hr at 5°C, most of the ether was evaporated in inert dry atmosphere, and the rest was decanted from the solid product and evaporated. Addition of dry petroleum ether gave yellow crystals. Sublimation or washing with small amounts of ether gave white powder which rapidly turned gray and then black and decomposed when touched with a metal spatula. The compound was kept under ether at -80° and used as early as possible after preparation for the kinetic experiments.[11]

Although we were unable to obtain a good elementary analysis for 3b[12] it was identified by the similarity of its $\lambda_{max}(CH_2Cl_2)$ at 270 nm (ε 7100) to that of 3a [$\lambda_{max}(CHCl_3)$ = 266 nm (ε 13,200)[9,13]]. Addition of MeOH and work-up gave a product with only a MeO singlet at δ 3.9, presumably due to $(NC)_2C=C(OMe)CN$. The strongest evidence for the structure is the reaction with N-alkylated anilines. Reaction with N,N-dimethylaniline gave immediately a violet solution with $\lambda_{max}(CH_2Cl_2)$ = 530 nm (ε ca. 40,000), a spectrum similar to that of 5a which was formed from 3a[10] or tetracyanoethylene[14] with N,N-dimethylaniline. Reaction with N-methylaniline gave the known yellow N-substitution product $PhNHC(CN)=C(CN)_2$,[14a] which was identified by its strong IR absorptions at 2220 cm^{-1} (conjugated C≡N) and 750 cm^{-1} (mono-substituted benzene ring) and the absence of an N-H absorption at 3400 cm^{-1}, by the signals at δ 3.8 (Me), 7.3, 7.95 (Ar) in the ^{1}H NMR spectrum and by the molecular peak at m/z 208 in the mass spectrum.

In the kinetic experiments freshly prepared solutions of 3a and 3b in $CHCl_3$ were injected into a $CHCl_3$ solution of excess of N,N-dimethyl, N,N-diethyl or 2,6-dimethylaniline which was kept in a thermostated cell of a Gilford 2400S spectrophotometer. The reaction was followed spectrophotometrically at the λ_{max} of the product. The concentration of 3b was calculated from the final absorption of the product. In the reaction with 2,6-dimethylaniline two maxima at 480 and at 350 nm were observed and followed. These were ascribed to the formation of both the p-substitution product, 2,6-dimethyl-4-tricyanovinylaniline (formed also in the reaction with tetracyanoethylene[15]) and the N-substitution product, since for $2,4,6\text{-}Me_3C_6H_2NHC(CN)=C(CN)_2$ $\lambda_{max}(EtOH)$ = 330 nm.[16]

All the reactions gave pseudo-first order kinetics. When the pseudo-first order constants were plotted vs. [Amine], linear plots with intercepts ≠ 0 were observed. Since it is not clear if the loss of 3a or 3b by an amine-independent reaction is real or an artefact, the k_{obs} values at each amine concentration are given in the Table. The k_{Br}/k_{Cl} ratios were calculated

Table. Substitution of 3a and 3b by Anilines in Chloroform

Amine	Conc., 10^4M	T,°C	10^4k_{obs},$M^{-1}s^{-1}$ for 3a	T,°C	10^4k_{obs},$M^{-1}s^{-1}$ for 3b	k_{Br}/k_{Cl}	
$PhNMe_2$ [a]	84	31.4	535	32.2	164	2.5	
	140		857		193	2.3	
	168		892		238	2.7	2.6±0.2[e]
	280		893		246	2.8	
$PhNEt_2$ [b]	11.2	32	890	31	201	2.3	
	33.6		890		197	2.2	
	56		1020		197	1.9	2.1±0.1[e]
	72.8				206		
	112		980			2.1	
$2,6\text{-}Me_2C_6H_3NH_2$ [c]	127.5	32	75	32	251	2.6	
	318				220	2.2	
	510		98				2.4±0.2[e]
	637		115		259	2.3	
	1275		102				
$2,6\text{-}Me_2C_6H_3NH_2$ [d]	68			35	88		
	204	32	49		147	3.0	
	510		78		353	4.5	3.8±0.8[e]
	1275		133				

[a] Followed at 515 nm. [b] Followed at 525 nm. [c] Reaction at the p-position. Measured at 480 nm. [d] Reaction at the nitrogen. Measured at 350 nm. [e] Average value.

from the Table by neglecting the somewhat different reaction temperatures, since the activation energies for the reactions of 3a are extremely low.[9]

Two important features emerge from the data: (a) The k_{obs} values at lower amine concentrations are lower than those at higher amine concentrations, especially for the substitution on nitrogen. This is reminiscent of the amine catalysis found in many nucleophilic vinylic substitutions of activated systems by amines[5] and may be due to the same reason.[17] (b) The average k_{Br}/k_{Cl} ratio is 2.37±0.18 for p-tricyanovinylation and 3.8±0.8 for N-tricyanovinylation. Consequently, even for the reaction of a highly activated system, where an intermediate zwitterion is undoubtedly formed, the k_{Br}/k_{Cl} ratio is only marginally higher, if at all, than the ratios found for much less activated systems. Moreover, if $k_{obs} = k_1k_{el}/k_{-1}$, and k_1/k_{-1} for 3b is slightly higher than, or similar to that for 3a as is customarily assumed, and if the proton transfer from 4 is not involved in the rate determining step as shown by isotope effect studies[9], the main mechanistic conclusion from the present work is that k_{el} of Br^- from 4b is only slightly higher, if at all, than k_{el} of Cl^- from 4a. This result is understandable only if the $\bar{C}\text{-}C\text{-}X \rightarrow C{=}C + X^-$ process involves an early transition state. This conclusion seems reasonable, in view of the fact that an early transition state for expulsion of poor nucleofuges was suggested for reactions of less activated systems,[18] whereas in expulsion of poor nucleofuges from highly activated systems the transition state is not so early.[19]

Due to the high activation for compounds 3 it is doubtful whether a higher k_{Br}/k_{Cl} or $k_{el}(Br)/k_{el}(Cl)$ ratio will be found for other multi-step nucleophilic vinylic substitutions. The discouraging conclusion is that in most cases the element effect cannot distinguish between a rate determining k_1 or k_{el} in the multi-step route. Whether it can distinguish between a multi-step and a single-step process which involves only a slight cleavage of the C-X bond in the transition state has to be determined by future experiments.

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(11) Although 3a is also unstable,[9,10] it is surprising that 3b is so much unstable, since the instability is attributed in part to the ease of nucleophilic C-X bond cleavage which does not differ much for 3a and 3b.

(12) Part of the sample decomposed before the analysis. The best analysis gave C, 35.4%, Br, 32.2%,Calcd. for 3b, C, 33%,Br, 43.9%.

(13) The lower ε for 3b may indicate decomposition or the presence of a non-absorbing impurity.

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(17) Indeed, the constancy of the third order rate constants for attack on the nitrogen is better than that of the second order k_{obs} values.

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(19) Deduced by the strong dependence of k_{el} on the nature of Y and Y' for highly activated systems. For collection of data see ref. 2a.

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