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THE POLAR REACTION CONSTANT FOR ALKENE CHLORINATION. SIMILARITY AND DIFFERENCES IN THE CHLORONIUM AND BROMONIUM ION LIKE TRANSITION STATES.

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Summary.- The polar reaction constant, $\rho^*_{Cl_2}$*, for the addition of free chlorine to alkenes, obtained in methanol at 25°C by direct kinetic methods, is -2.9 whereas* $\rho^*_{Br_2}$ *is -3.1. The change from bromination to chlorination is associated with a large reactivity increase but a small drop in selectivity. This result is discussed in terms of the Hammond postulate and dependence of the charge distribution on the bridging atom in the halonium transition states.*

In view of the current interest in predicting reaction selectivity (1), it would be instructive to have comparable data on alkene bromination and chlorination, since chlorination is about two powers of ten faster than bromination (2). Whereas there are abundant data concerning bromination, chlorination is poorly documented; moreover, the few data which are available are rather disconcerting.

In particular, there are at present four values (3) of the polar reaction constant, $\rho^*_{Cl_2}$; depending on solvent, substituent or temperature, they range from -1.0 to -4.1. This diversity is astonishing because for bromination $\rho^*_{Br_2}$ is -3.1, independent of the substituents and the solvent (4). We must conclude, therefore, either that some $\rho^*_{Cl_2}$ - values are wrong or that bromination and chlorination proceed through very different mechanisms.

The first proposition is not unreasonable since the kinetic data used for the calculation of $\rho^*_{Cl_2}$ have not always been obtained by reliable methods. To measure the generally high chlorination rate constants, various devices have been used either to slow down the reaction by using low temperatures and/or deactivating double bond substituents or by means of competitive method to avoid fast kinetic measurements. Now, it has been shown that competitive methods lead frequently to a contraction in the reactivity ranges (5).

To eliminate errors of this type, we set out to collect kinetic data directly by adapting the most reliable current techniques designed for bromination. By couloamperometry (6) in particular, bromination can be followed up to rate constants as high as 10^8 $M^{-1}s^{-1}$. We have, therefore, adapted this technique to chlorination (7).

TABLE : EXPERIMENTAL CHLORINATION RATE CONSTANTS OF OLEFINS $CH_2=CH-CH_2X$, IN METHANOL AT 25°C.

N°	X	$[H^+]$ [a]	$[Cl^-]$ [a]	k_{exp} [b,c]	k_{Cl_2} [b]	k_{Br_2} [b,d]
1	Et [e]	10^{-4}	10^{-1}	1.2×10^4	1.25×10^4	4.5×10^2
		5×10^{-4}	"	1.4×10^4		
		10^{-3}	"	1.5×10^4		
		"	5×10^{-2}	1.3×10^4		
		"	2×10^{-1}	1.7×10^4		
2	Ph [e]	10^{-4}	10^{-1}	2.3×10^3	2.8×10^3	5.3×10^2
		5×10^{-4}	"	3.1×10^3		
		10^{-3}	"	3.2×10^3		
		"	5×10^{-2}	$2.9. \times 10^3$		
		"	2×10^{-1}	$3.4. \times 10^3$		
3	OCOMe [e,f]	5×10^{-4}	10^{-1}	47.7	48.5	8.5×10^{-1}
		10^{-3}	"	55.0		
		"	5×10^{-2}	50.8		
		"	2×10^{-1}	59.6		
4	Cl [e,f]	10^{-4}	10^{-1}	11.0	9.4	1.7×10^{-1}
		5×10^{-4}	"	12.2		
		10^{-3}	"	12.6		
		"	5×10^{-2}	10.1		
			2×10^{-1}	14		

a) M b) k in $M^{-1}s^{-1}$ c) ± 3% d) From Ref. 4a e) couloamperometry f) spectrokinetic

The $\rho^*_{Br_2}$ -value has been obtained in methanol from data on olefins with non-conjugating substituents whose polar effects vary widely whereas their steric effect is practically constant (4a). We choose, therefore, the same olefins and the same solvent to determine $\rho^*_{Cl_2}$.

To make sure that chlorination rate constants are related to a mechanism similar to that of bromination, it is necessary that these constants correspond to the addition of free chlorine only. This restriction is imperative because the halogenated species in methanolic solutions containing halide ions differ from bromine to chlorine.

In the case of bromine (8), the predominant species are free bromine and tribromide ion whereas for chlorine (9), they are free chlorine and methoxychloride.

$$X_2 + X^- \rightleftharpoons X_3^- \qquad (1)$$

$$X_2 + MeOH \rightleftharpoons XOMe + H^+ + X^- \qquad (2)$$

To reduce the importance of the methoxychloride in chlorination, our experimental work has been carried out under acidic conditions, as shown in the Table. The bromination rate constants, k_{Br_2}, are calculated by extrapolating the kinetic bromide ion effects to $[Br^-] = 0$; chlorination rate constants, k_{Cl_2}, should be obtained by extrapolating both acid and chloride ion effects.

Kinetic results are given in the Table. Experimental acid and chloride ion effects are expressed by the classical equations (10,11):

$$k_{exp} = k_o^{H^+} (1 + a [H^+]) \qquad (3)$$

$$k_{exp} = k_o^{Cl^-} (1 + b [Cl^-]) \qquad (4)$$

The rate constants, $k_o^{H^+}$ and $k_o^{Cl^-}$ are identical. It is, therefore, reasonable to identify them as k_{Cl_2}, the rate constant for the addition of free chlorine alone.

There is a very good linear relationship, with a near unit slope, between the bromination and chlorination rates for the four olefins of the Table. We obtain the $\rho^*_{Cl_2}$-value from the slope of eq. 5 and the $\rho^*_{Br_2}$ value established previously (4a) from data covering a larger

$$\log k_{Cl_2} = 0.92 \log k_{Br_2} + 1.74 \qquad (5)$$

$$(R=0.998, \quad s=0.11)$$

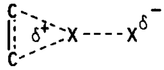
reactivity range (9.5 log.units).

$$\rho^*_{Br_2} = -3.10 \qquad \rho^*_{Cl_2} = -2.9$$

This $\rho^*_{Cl_2}$ value closely resembles that calculated from Shelton's data measured by a direct spectrokinetic method (3a). In contrast, it differs markedly from that found (3d) by V'yunov also based on direct kinetic measurements; this may be due to the use of a different medium, CCl_4 whose ionizing power is much smaller than that of methanol and/or to the small reactivity range covered by the Rusian data (0.5 *ℓ.u.* compared to 3.1 *ℓ.u.* in methanol). The other $\rho^*_{Cl_2}$-values have been obtained by competitive methods and their smallness is in agreement with previous findings regarding these indirect methods. Poutsma's highly negative value (3b) is hard to understand but could be due to temperature differences, since this work is carried out at -9°C rather than 25°C.

Whatever the reasons for divergences in the literature concerning $\rho^*_{Cl_2}$-values, it is reasonable to adopt our new value because it is based on reliable kinetic data, because these data cover a large reactivity range, because they concern only free chlorine addition and finally, because it is compatible with $\rho^*_{Br_2}$.

Since chlorination is faster than bromination, an earlier transition state is expected. This Hammond effect (12) adequately explains the variation in selectivity for electrophilic halogenation of benzenes: ρ^+ changes from -12.0 to -9.6 on going from bromination (13) to chlorination (14). If these data are transposed to electrophilic additions to alkenes, one would expect a $\rho^*_{Cl_2}$-value of -2.5 at the most, i.e. smaller than that which we obtain. However, in the case of alkene additions, the Hammond effect can be partially compensated by a modification of the charge distribution in the transition state when the bridging atom goes from bromine to chlorine (15).



It is known that chlorine atom is a poor neighbouring group as compared to bromine (16). Therefore, whereas the total charge of the chloronium transition state is smaller than that of the bromonium, the charge carried by the carbon atoms and upon which olefinic substituent effects depend could be almost identical. *The association of the two effects, Hammond and charge distribution, explains* why $\rho^*_{Cl_2}$ is only slightly less than $\rho^*_{Br_2}$ despite the large reactivity difference between the two halogens. This result is a further example of compensation between opposite effects on reactivity, which appears to be the most frequent reason for violation of the Reactivity-Selectivity Principle (17). Work is in progress to acquire more information about transition state structures in these closely-related electrophilic additions.

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