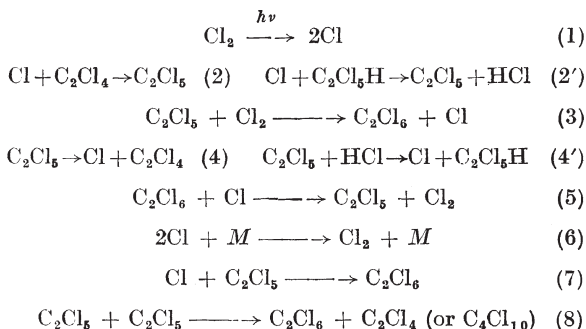


Competition in Atomic Halogenation Reactions

It has been shown recently¹ that it is useful to consider a general mechanism for atomic halogenation reactions, which, in the case of the photochlorination of C₂Cl₄ and C₂HCl₃, is given by :



It has also been shown that the usual steady-state treatment is adequate for calculating overall rate equations², and that absolute reaction-rate theory and rough estimates of activation energies and entropies permit one to calculate approximately the overall rate constants¹.

The rate of substitution (*D1*, Table 1) and of several competition reactions (*A2*, *E*, *F*, *G*) have now been measured³ and are summarized in the table with the previously measured rates of addition (*A1*, *B*) and of dehydrochlorination (*C*)¹. Table 1 shows further that several overall rate constants which are measured directly may equally well be calculated from other measurements. The good agreement between these direct and indirect determinations is an extremely satisfactory control of the accuracy of the proposed mechanism; it shows further that the error limits for activation energies and frequency factors are extremely narrow.

Further, as shown in Table 1, the life-time of the reaction chain in the addition reaction at low temperature (*H*) yields values of three rate constants of elementary steps (*H*, *I*, *J*).

We intend to measure further the life-time of the reaction chain of the addition reaction at high temperature and of the dehydrochlorination, as well as further competition reactions, and to calculate the equilibrium constants. This should yield values for the eight rate constants which determine the reaction mechanism. A discussion of the measured values of activation energies and entropies in terms of reaction-rate theory will be useful after several similar systems have been studied (C₂HCl₃ - C₂H₂Cl₄; C₂H₂Cl₂ - C₂H₃Cl₃; etc.).

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² Adam, J., Dusoleil, S., and Goldfinger, P., *Bull. Soc. Chim. Belg.*, **65**, 942 (1956).
³ Ackerman, M., Chiltz, G., Goldfinger, P., and Martens, G., *Bull. Soc. Chim. Belg.* (in the press).

Gas-Chromatographic Analysis of Higher Fatty Acids; up to and including Cerotic Acid

THE rapid gas-chromatographic analysis of fatty acid methyl esters was applied by Cropper and Heywood¹ and by Dijkstra, Keppler and Schols² to the saturated fatty acids up to and including behenic acid. James and Martin³ and James and Wheatley⁴ analysed unsaturated and saturated fatty acid methyl esters up to and including a C₁₅-acid.

Table 1. CORRELATION BETWEEN THE RATE CONSTANTS OF CHLORINATION AND DEHYDROCHLORINATION OF C₂CL₄ AND C₂CL₅H AND OF COMPETITION BETWEEN THESE REACTIONS

Type of rate measurement or combination of measurements	Rate equation	Temperature interval	Value of log (rate constants representing directly measured rates)	Value of log (rate constants giving best agreement between directly measured and calculated rate constants)
A. (1) addition at low temperature Cl ₂ + C ₂ Cl ₄ (2) reaction of Cl ₂ with a mixture C ₂ Cl ₄ + C ₂ Cl ₅ H (3) from substitution (<i>D1</i>)	$(Ia^{1/2}k_2/k_3^{1/2})(Cl_2)^{3/2}$	360°-430° K.		
B. addition at high temperature dehydrochlorination	$Ia^{1/2} k_2(k_2/k_4k_7)^{1/2}(Cl_2)(C_2Cl_4)^{1/2}$ $(Ia'k_2'/k_4/k_7)^{1/2}(C_2Cl_5H)^{1/2}$	370°-390° K. 370°-430° K. 520°-560° K. 400°-470° K.	- 660/T + 2.56 + 1,800/T - 1.17 - 2,500/T + 6.20	- 660/T + 2.56 + 1,725/T - 1.20 - 2,450/T + 6.20
C. (1) $(k_2k_4/k_7)^{1/2}$ {from substitution (2) $B.E.^{1/2}$	$Ia^{1/2}(k_2k_4/k_7)(Cl_2)/k_2'(C_2Cl_5H) + k_8)^{-1/2}k_3(Cl_2)$	370°-430° K.	- 800/T + 3.12	- 675/T + 3.05
E. (1) from equality of addition and dehydrochlorination (2) $(D/E)^2$	$k_2k_2'(C_2Cl_5H) = k_2k_3(C_2Cl_4)(Cl_2)$	400°-430° K.	- 4,600/T + 8.46	- 4,800/T + 8.50
F. (1) competition substitution— dehydrochlorination (2) $(C/D)^2$	$k_4/k_3(Cl_2)$	400°-430° K.	- 2,890/T + 4.98	- 3,550/T + 6.30
G. (1) competition addition substitu- tion (2) $(B.C/D)^2$ (3) $(C/B.E)^2$ (4) F/E	$k_2(C_2Cl_4)/k_2'(C_2Cl_5H)$	365°-385° K.	+ 1,400/T - 2.28	+ 1,250/T - 2.20
H. Cl ₂ + C ₂ Cl ₄ at low tempera- ture in intermittent light	$k_3^{1/2}$	360°-420° K.	- 150/T + 4.6	- 150/T + 4.6
I. A.H.	k_3			- 810/T + 7.2
J. I.F.	k_4			- 4,360/T + 13.5