Chromyl Chloride Oxidations. IV.[1,2] Kinetics and Mechanism of the Addition to Styrene

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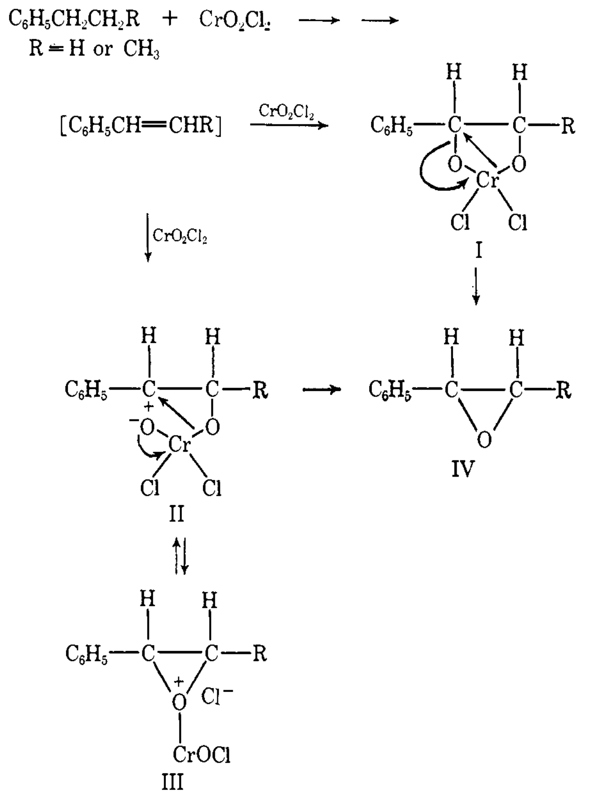
Abstract: The kinetics of the chromyl chloride addition to (oxidation of) the carbon–carbon double bond of styrene, to give the chromyl chloride–styrene adduct, have been investigated *via* spectrophotometric stopped-flow techniques. The reaction is overall second order, first order in each reactant. A correlation of σ^+ substiutent values and rate constants has been obtained for the substituents p-CH$_3$, p-C$_6$H$_5$, H, p-Cl, p-Br, m-Cl, and m-NO$_2$ with $\rho = -1.99$. $\Delta H^{\ddagger}$ is 8.4 kcal/mol, and $\Delta S^{\ddagger}$ is -23.8 eu. The data are consistent with a mechanism which involves an electrophilic attack of chromyl chloride at the carbon–carbon double bond to give either a partially bridged resonance-stabilized five-membered-ring activated complex or an epoxide-like cyclic three-membered-ring activated complex in the rate-determining step.

Although numerous studies have been devoted to the oxidation of alkenes and styrenes by chromyl acetate and chromic acid,[4] no kinetic studies of the chromyl chloride oxidation of styrenes have appeared.[1,5–9] Cycloalkenes[10] and styrenes[11] have been postulated as intermediates in the chromyl chloride oxidation of cycloalkanes and arylalkanes (Étard reaction),[4,6b,12,13] respectively. The intermediacy of styrenes in the Étard reaction has been recently demonstrated.[1,6b,9,11] Intermediates I–III have been suggested to account for the variety of products from arylalkanes and unsaturates (Scheme I).[1,4,6–9] III was invoked to explain the formation of chlorohydrins in the oxidation of alkenes and cycloalkenes.[5,8,14–16] Also, it is possible for I or II to rearrange to the epoxide (IV) which can isomerize to the observed carbonyl products during the acidic hydrolysis step.

Scheme I



Owing to the absence of previous kinetic studies, this investigation was undertaken in order to gain a clearer understanding of the mechanism of the chromyl chloride addition to (oxidation of) styrene, and of the properties of resulting activated complex. We now report the results of a spectrophotometric stopped-flow study of the chromyl chloride oxidation of styrene (V).

Experimental Section

Uv spectra were taken on a Beckman DK-2A spectrophotometer.

Reagents. The styrenes were obtained commercially: styrene (Matheson), m-NO$_2$, p-Br, p-Cl, p-CH$_3$, and p-C$_6$H$_5$ styrenes (Aldrich), and p-OCH$_3$ styrene (K & K Laboratories). Chromyl chloride (Alfa Inorganics), styrenes, and specially purified CCl$_4$ were distilled and/or recrystallized immediately before use.

Specially Purified Carbon Tetrachloride. A mixture of 1 l. of reagent or technical grade CCl$_4$ and 3.82 g (0.025 mol) of chromyl chloride was allowed to stand at room temperature for 3 days in a dark closed container.[17] The resulting mixture was treated with 3.3 g (0.05 mol) of 90–95% technical zinc dust (Allied),[18] stirred

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[1] Part III: F. Freeman and N. J. Yamachika, *Tetrahedron Lett.*, 3615 (1969).

[2] Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 11, 1969.

[3] Petroleum Research Fund Scholar, 1968–1970.

[4] The subject has been reviewed by K. B. Wiberg, "Oxidation in Organic Chemistry," Part A, Academic Press, New York, N. Y., 1965, p 69 ff.

[5] W. H. Hartford and M. Darren, *Chem. Rev.*, **58**, 1 (1958).

[6] (a) F. Freeman, P. J. Cameron, and R. H. DuBois, *J. Org. Chem.*, 33, 3970 (1968); (b) F. Freeman, R. H. DuBois, and N. J. Yamachika, *Tetrahedron*, **25**, 3441 (1969).

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[14] S. J. Cristol and K. R. Eilar, *J. Amer. Chem. Soc.*, **72**, 4353 (1950).

[15] C. N. Rentea, I. Necsoiu, M. Rentea, A. Ghenciulescu, and C. D. Nenitzescu, *Tetrahedron*, 22, 3501 (1966).

[16] Curiously, it appears that only straight-chain alkenes, cyclohexene, and cyclopentene give chlorohydrins.[5,8,14] In contrast, 1,1-disubstituted alkenes give good to excellent yields of aldehydes and ketones.[6] Presumably, chlorohydrins are formed during isolation of the adduct or when an excess of chromyl chloride is used.

[17] It was found that 1 day was not sufficient to remove the impurities.

[18] Caution: *Although we have not experienced any difficulties, it is possible that the finely divided zinc metal may ignite spontaneously with air when damp.*

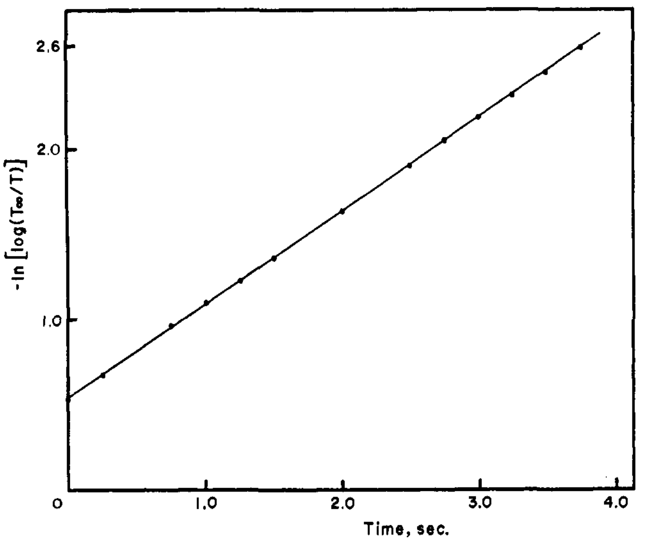

Figure 1. A typical pseudo-first-order plot. The conditions are $[CrO_2Cl_2] = 4 \times 10^{-4}$ *M*, [styrene] $= 16 \times 10^{-3}$ *M*, λ 415 mμ, $T = 15.0°$.

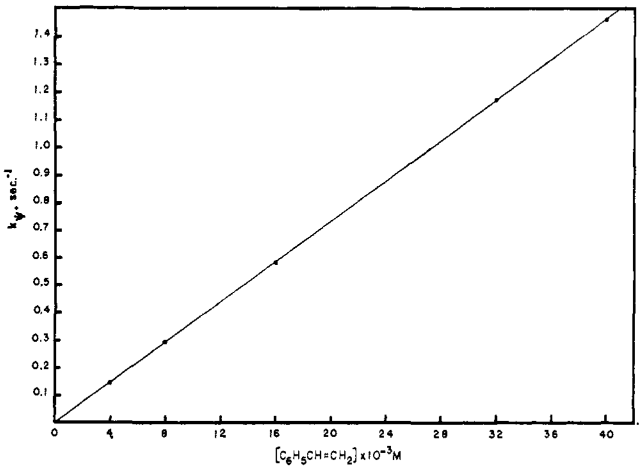

Figure 2. Effect of styrene concentration on the pseudo-first-order rate constants for the chromyl chloride oxidation of styrene at 15.0°.

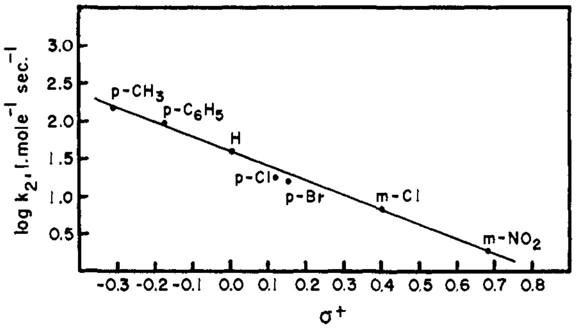

Figure 3. Hammett correlation of rates of oxidation by chromyl chloride with σ^+.

5 min, and then 30 g of ice, 30 g of water, and 25 ml of 6 *N* HCl were added. After stirring for 10 min, the mixture was separated and the organic layer was washed with 200 ml of dilute NaOH, with 200 ml of dilute HCl, and then three times with 100-ml portions of distilled H_2O. The CCl_4 was dried over $CaCl_2$ for 2 days and filtered, and the filtrate was distilled at 76.8–77.0° through a 4-ft bubble-chamber column.

Kinetic Measurements. Because of the short reaction time, the rates were determined by following the disappearance of chromyl chloride (415 and 440 mμ) with a stopped-flow reactor[19-21] in a Beckman DU spectrophotometer under pseudo-first-order rate conditions (large excess of styrene). The rate pseudo-first-order constants (k_ψ) were obtained from the slopes of plots of $-\ln$ [log (T_∞/T)] *vs.* time (Figure 1) where T_∞ is the per cent transmission at a point just before the styrene–chromyl chloride adduct begins to form (after at least two half-lives), and were calculated on an IBM 1620 computer.[24] All rate constants given in the tables are the average of two or more determinations, and the deviations are the *mean* deviations for the set of runs. The small deviations suggest a reasonably good degree of accuracy and precision.

Results

Stoichiometry. Chromyl chloride reacts rapidly with V to give the chromyl chloride–styrene adduct (VI) which has been shown to have the approximate composition $C_8H_8\cdot CrO_2Cl_2$.[9,25,26] Although the structure of VI has not been fully elucidated, it yields phenylacetaldehyde (VII) and benzaldehyde (VIII) as the major oxidation products on hydrolysis.[9] A cationic intermediate during hydrolysis is suggested by the structurally rearranged product VII, which probably results from a hydride transfer, while VIII presumably arises from cleavage of the carbon–carbon double bond of V by chromic acid during hydrolysis.[1,4,27]

$$\underset{\mathrm{V}}{\mathrm{C_6H_5CH{=}CH_2}} + \mathrm{CrO_2Cl_2} \xrightarrow[\mathrm{CCl_4}]{0^\circ} \underset{\mathrm{VI}}{[\mathrm{C_8H_8\cdot CrO_2Cl_2}]} \qquad (1)$$

$$\mathrm{VI} \xrightarrow{\text{hydrolysis}} \underset{\substack{(76.5\%)\\ \mathrm{VII}}}{\mathrm{C_6H_5CH_2CHO}} + \underset{\substack{(21.1\%)\\ \mathrm{VIII}}}{\mathrm{C_6H_5CHO}} + \underset{(2.4\%)}{\mathrm{C_6H_5COCH_3}} \qquad (2)$$

Kinetic Data. The kinetic data for the chromyl chloride oxidation of V are summarized in Table I. A plot (Figure 2) of k_ψ *vs.* a tenfold range of concentration of V gives a straight line that passes through the origin indicating the rate of oxidation to have a first-order dependence on V. This is further demonstrated by the constancy of k_2 (Table I). At constant styrene concentration (large excess), the pseudo-first-order rate constant (k_ψ) did not alter appreciably with changing chromyl chloride concentrations (sixfold range) which indicates a first-order dependence on chromyl chloride. These data suggest the following rate law

$$\frac{-\mathrm{d}[\mathrm{CrO_2Cl_2}]}{\mathrm{d}t} = k[\text{styrene}][\mathrm{CrO_2Cl_2}] \qquad (3)$$

Linear Free Energy Relationship. Although the rate of oxidation of *p*-methoxystyrene was too fast to be measured in this stopped-flow system, the rates of oxidation of six ring-substituted styrenes were determined (Table II). Correlation of the rate constants with σ^+ substituent constants gave a ρ of -1.99.[28,29] The correlation coefficient (r) was 0.9961, and the standard deviation (s) from the regression line was 0.0576 (Fig-

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(19) (a) K. B. Wiberg and R. D. Geer, *J. Amer. Chem. Soc.*, **87**, 5202 (1965); (b) K. B. Wiberg and R. D. Geer, *ibid.*, **88**, 5827 (1966).

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(21) Chromyl chloride has an uv max at 290 mμ (ε 3600) and a visible max at 415 mμ (ε 2900).[22,23]

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Table I. Kinetic Data for the Chromyl Chloride Oxidation of Styrene at 15°

[Styrene] × 10^3 M	[CrO_2Cl_2] × 10^4 M	k_ψ[a] × 10^2 sec^{-1}	k_ψ/[styrene] = k_2, M^{-1} sec^{-1}	
4.0	4.00[b]	14.6 ± 0.4	36.6	37.1 ± 0.5
8.0	4.00[b]	30.0 ± 0.3	37.5	
16.0	4.00[b]	58.7 ± 0.2	36.7	
32.0	4.00[b]	117.5 ± 2.6	36.7	
40.0	4.00[b]	146.7 ± 9.5	36.7	
16.0	2.00[c]	54.6 ± 0.6	34.1	36.9 ± 2.8
16.0	4.00[c]	61.7 ± 1.0	38.5	
16.0	6.00[c]	59.2 ± 0.0	37.0	
16.0	8.00[c]	61.1 ± 0.06	38.2	
16.0	12.00[c]	63.4 ± 5.0	39.6	

[a] Pseudo-first-order rate constant. [b] λ 415 mμ. [c] λ 440 mμ.

Table II. Effect of Ring Substitution on the Rate of Chromyl Chloride Addition at 15° [a]

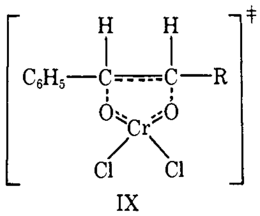
Substituent	k_2, M^{-1} sec^{-1}
p-Methyl	150.6
p-Phenyl	98.5
Hydrogen	36.6
p-Chloro	17.7
p-Bromo	16.5
m-Chloro	6.95
p-Nitro	1.69
p-Methoxy[b]	

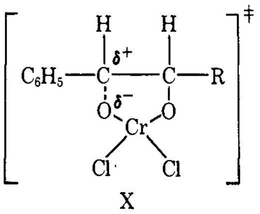
[a] λ 415 mμ. [b] Too fast to be measured.

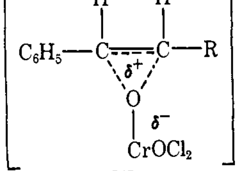
ure 3). Correlation with Hammett's σ substituent constants gave a ρ of -1.21 with $r = 0.9774$ and $s = 0.1548$.

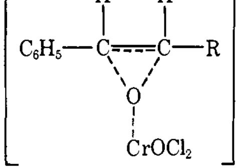
Discussion

The kinetic behavior described above is consistent with a mechanism involving a rate-determining reaction between chromyl chloride and V. This suggests that the activated complex of the rate-controlling step consists of the elements of styrene (V) and either the elements of chromyl chloride or the elements of something that has a concentration proportional to that of chromyl chloride. The rate data are also consistent with a transition state which involves partial bonding of the chromyl chloride molecule with one or both termini of the unsaturated system with little or no development of positive charge on the benzylic carbon. Therefore, IX, X, XI, and XII merit consideration as the possible rate-limiting activated complex of formation of the styrene–chromyl chloride adduct (VI).


IX


X


XI


XII

Possibly a slow step for a concerted *cis*-1,3-cycloaddition of chromyl chloride to the carbon–carbon double bond of V could be represented by IX. However, the activated complex for the formation of the styrene–chromyl chloride adduct (VI) probably cannot have a very close resemblance to IX since the rate of oxidation is increased by electron-donating substituents and decreased by electron-withdrawing groups ($\rho = -1.99$). Wiberg and Geer[19b] have shown that the permanganate oxidation of substituted cinnamic acids, which presumably proceeds *via* a *cis*-cycloaddition mechanism, has a ρ value close to zero. Furthermore, 1,3-dipolar cycloaddition reactions are generally characterized by small positive ρ values (+0.8).[30,31] Consequently, the magnitude of the observed ρ value (-1.99) makes IX an unreasonable activated complex for the chromyl chloride oxidation of V.

A fully developed benzylic carbonium ion-like activated complex probably is not involved in the slow step because of the small value of the observed ρ. ρ values larger than -3 generally suggest a fairly large degree of carbonium ion character in the activated complex (Table III). Consequently, the partially bridged resonance-stabilized five-membered-ring activated complex X and the epoxide-like cyclic three-membered ring activated complexes XI and XII are entirely compatible with the kinetic data.[32] A small value of ρ would be expected for the formation of X, XI, or XII in the slow step. Correlation of epoxidation rates for ring-sub-

Table III. Reaction Constants for Some Carbonium Ion Reactions

Reaction	ρ	Ref
Solvolysis of 2-phenyl-2-propyl chlorides	−4.54	28
Addition of chlorine to cinnamic acids	−4.01	*a*
Hydration of α-methylstyrenes	−3.4	*b*
Hydration of styrenes	−3.2	*c*
Solvolysis of *t*-cumyl chlorides	−4.67	*d*
Bromination of styrenes	−4.30	*e,f*

[a] H. P. Rothbaum, I-Ting, and P. W. Robertson, *J. Chem. Soc.*, 980 (1948). [b] W. M. Schubert, B. Lamm, and J. R. Keefe, *J. Amer. Chem. Soc.*, **86**, 4727 (1964). [c] N. C. Deno, F. A. Kish, and H. J. Peterson, *ibid.*, **87**, 2157 (1965). [d] Y. Okamoto, T. Inukai, and H. C. Brown, *ibid.*, **80**, 4972 (1958). [e] J. E. Dubois and A. Schwarcz, *Tetrahedron Lett.*, 2167 (1964). [f] J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1483 (1969).

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(30) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 633 (1963).

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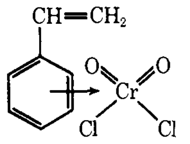
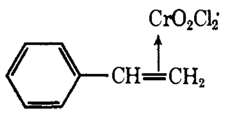
(32) It is noted that the kinetic data are not inconsistent with the formation of the charge-transfer complex XIII or the π complex XIV in the rate-determining step.



XIII

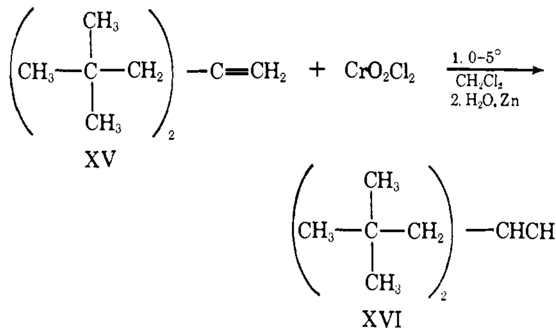


XIV

stituted styrenes with σ^+ gives a ρ value of -1.3[33] which is close to the observed value for the chromyl chloride oxidation. The activation parameters for the oxidation of V, $\Delta H^\ddagger = 8.4$ kcal/mole and $\Delta S^\ddagger = -23.8$ eu, are also consistent with the formulation of X, XI, or XII in the rate-limiting step since 1,3-dipolar cycloadditions and epoxidations require a high degree of order in the activated complex. In cycloadditions $\Delta S^\ddagger$ values of -25 to -35 eu are generally observed,[30,34] and in epoxidations $\Delta S^\ddagger$ values of -21 to -26 eu are obtained.[33-35]

The foregoing conclusions lend support to the suggestion that the mechanism of the chromyl chloride oxidation of V involves an electrophilic attack of chromyl chloride at the carbon–carbon double bond in the rate-determining step to give X, XI, or XII. Furthermore, it is possible that X could also be the activated complex of a rearrangement step to the postulated product-determining intermediate I or II, and that XI or XII could lead directly to the epoxide IV which isomerizes to the observed carbonyl products.

The activated complexes XI and XII also appear to be plausible for the chromyl chloride oxidation of alkenes.[6a] For example, 4,4-dimethyl-2-neopentyl-1-pentene (XV), on treatment with chromyl chloride (followed by reductive hydrolysis), gives an 81% yield of 4,4-dimethyl-2-neopentylpentanal (XVI), while it is inert to hot concentrated alkaline permanganate.[36] Presumably the bulky neopentyl groups preclude the typical *cis*-cycloaddition of permanganate to the carbon–carbon double bond.[37-40] In contrast to its inertness to permanganate, XV forms epoxides with chromyl acetate[41] and perbenzoic acid.[36,40]



XV

XVI

(4)

Acknowledgment. We express our deep appreciation for support of this work to the Research Corporation and to the donors of the Petroleum Research Fund administered by the American Chemical Society. Our thanks also go to Professor James L. Jensen for helpful discussions.

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(37) XV is not readily attacked by chromic acid[38] or bromine.[32]

(38) See Table III, footnote *f*.

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N-Phosphorylated Aziridines. The Reaction of 2-Iodoalkyl Azides with Phosphines and Phosphites[1]

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Abstract: 2-Iodoalkyl azides react readily and stereospecifically with trivalent phosphorus nucleophiles by attack on azide to form N-phosphorylated aziridines. The use of triphenylphosphine gives aziridinyltriphenylphosphonium iodide salts **5**. When phosphites were used these salts underwent further transformations *in situ* leading to aziridinephosphonates **7**, **10**, or **11**. The structure of these compounds was proved by an independent synthesis. LAH reduction of **5** or **7** proceeded with P–N bond cleavage. This reaction sequence was shown to be a convenient method of aziridine synthesis in particular for cases where other methods failed. Dimethyl N-(2,2-diphenylaziridinyl)phosphonate **20** rearranges on standing to an enamine phosphonate **23**. The use of nmr in distinguishing between aziridinyl and open chain isomers is discussed.

We have previously reported the synthesis of 2-iodoalkyl azides[2] from olefins and their subsequent transformation among others into vinyl azides,[3] azirines,[4] and aziridines.[5] We now wish to report the reaction of 2-iodoalkyl azides with trivalent phosphorus compounds.

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