the mixture was stirred 1 additional hr while warming to room temperature. After removal of the amine salt by filtration, the solvent was evaporated and the *endo-/exo*-isopropyl isomer distribution was 2.8 as indicated by vpc. Vacuum distillation through a 6-in. Vigreux column yielded 37 g of crude product (78%) at 61–73° (0.1 mm). The isomer distribution had not changed after distillation. The isomers were separated by vpc and both isomers showed the characteristic carbonyl absorptions in the ir at 1800 cm^{-1} (s) and carbon–carbon unsaturation at 1607 cm^{-1} (w). That portion of the nmr spectrum not recorded in Table II is as follows: (*endo*-isopropyl isomer) δ 1.9 (m, 1 H), 1.0 (d, 3 H), and 1.1 (d, 3 H).

Anal. Calcd for $C_{10}H_{13}OBr$: C, 52.24; H, 5.77. Found: C, 52.30; H, 5.67.

2-Bromo-3,3-dimethylbutanoyl Chloride. A solution consisting of 126 g (1.0 mol) of 3,3-dimethylbutanoic acid, 160 g (1.0 mol) of bromine, and 5 ml of phosphorus trichloride was heated at 70–80° for 24 hr or until the reaction mixture no longer showed the red color of bromine. The reaction solution was cooled in an ice bath and treated with 207.5 g (1.0 mol) of phosphorus pentachloride. Upon heating at reflux for 2 hr, the crude acid chloride could be removed by distillation at 108–110° (30 mm) to yield 138 g (61%), nmr (CCl_4) δ 4.42 (s, 1 H) and 1.18 (s, 9 H).

7-Bromo-7-(2-methyl-2-propyl)bicyclo[3.2.0]hept-2-en-6-one. The dehydrochlorination of 2-bromo-3,3-dimethylbutanoyl chloride with triethylamine in the presence of cyclopentadiene was conducted by the same general procedure as described above. The cycloadduct was distilled through a 24-in. Vigreux column at 66–67° (0.4 mm): ir 1800 (C=O) and 1607 cm^{-1} C=C); nmr other than that described in Table II, δ 1.12 (s, 9 H). Only one isomer, the *endo-t*-butyl isomer, was obtained as evidenced by nmr and vpc.

Anal. Calcd for $C_{11}H_{15}OBr$: C, 54.3; H, 6.17; mol wt, 243. Found: C, 54.54; H, 6.19; mol wt (by mass spectroscopy), 243.

7-Methyl-7-propylbicyclo[3.2.0]hept-2-en-6-one. The same general procedure was employed as described above for the dehydrochlorination of 2-methylpentanoyl chloride with triethylamine in the presence of cyclopentadiene. The cycloadduct distilled at 95–98° (2.5 mm): ir 1800 (C=O) and 1609 cm^{-1} (C=C); nmr other than that described in Table II, δ 1.4 (m, 4 H) and 1.05 (m, 3 H). An *endo-/exo-n*-propyl isomer distribution of 1.4 was obtained as evidenced by the nmr spectrum and vpc of the reaction solution prior to distillation.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.4; H, 9.80. Found: C, 80.2; H, 10.17.

Other Cycloadditions. All the other cycloadditions were effected as previously described except for changing the solvent and/or temperature.

Acknowledgment. Support for this investigation by the Robert A. Welch Foundation and the National Science Foundation (GP-7386) is gratefully acknowledged. The authors also wish to express their gratitude to Professor Roald Hoffmann for private communications concerning these results.

Chromyl Chloride Oxidations. V. Kinetics and Mechanism of the Electrophilic Addition to Alkenes[1,2]

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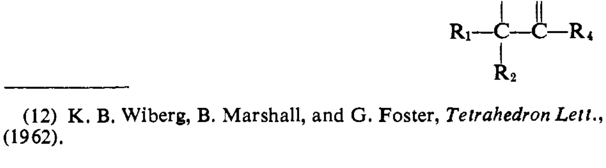
Received December 31, 1969

Abstract: The kinetics of the chromyl chloride oxidation of 15 alkenes, to give the chromyl chloride–alkene adduct, have been studied by spectrophotometric stopped-flow techniques. A first-order dependence on the concentration of each reactant was observed. The reactions are little affected by steric factors and are characterized by low enthalpies of activation ($\Delta H^{\ddagger}$ = 5.4–7.2 kcal/mol) and large negative entropies of activation ($\Delta S^{\ddagger}$ = −27.4 to −40.7 eu). An increase in alkyl substitution at the carbon–carbon double bond leads to large rate enhancements. An excellent correlation is obtained with Taft's σ^* values, and good correlations are also obtained with various forms of the extended Hammett equation. Comparison of the relative reactivities of chromyl chloride oxidations with other electrophilic alkene reactions (bromine and chlorine addition, chromic acid oxidation, epoxidation) suggest that the rate-determining step involves a partially positive charged cyclic three-membered ring activated complex.

The nature of the products from the chromyl chloride oxidation of carbon–carbon double bonds in alkenes,[5–7] cycloalkenes,[8–10] and styrenes[9,11,12] has been a subject of great controversy in recent years. For example, it has been reported that excess chromyl chloride oxidizes alkenes to chlorohydrins in low yields.[5,6] However, more recent product studies[7] (Table I) have shown that when a 1:1 molar ratio of chromyl chloride and alkene is used, the major oxidation products are carbonyl compounds which arise from hydride or alkyl migration (eq 1). In order to



(1)

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(1) Previous paper in series: F. Freeman and N. J. Yamachika, *J. Amer. Chem. Soc.*, in press.

(2) Presented in part before the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 25, 1970.

(3) Abstracted in part from the M.S. thesis of P. D. McCart, California State College, Long Beach, Calif., 1969.

(4) Petroleum Research Fund Scholar, 1968–1970.

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

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

(7) F. Freeman, P. J. Cameron, and R. H. DuBois, *J. Org. Chem.*, **33**, 3970 (1968).

(8) R. A. Stairs, D. G. M. Diaper, and A. L. Gatzke, *Can. J. Chem.*, **41**, 1059 (1963).

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

(10) F. Freeman and N. J. Yamachika, unpublished results, 1969.

(11) F. Freeman, R. H. DuBois, and N. J. Yamachika, *Tetrahedron*, **25**, 3441 (1969).

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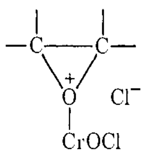
Table I. Oxidation of Substituted Ethenes with Chromyl Chloride

Ethene	Product(s)	% yield
4,4-Dimethyl-2-neopentyl-1-pentene	4,4-Dimethyl-2-neopentylpentanal	80.8[a]
2,4,4-Trimethyl-1-pentene	2,4,4-Trimethylpentanal	75.8[a]
2,3,3-Trimethyl-1-butene	2,3,3-Trimethylbutanal	34.9[a]
2,3-Dimethyl-2-butene	3,3-Dimethyl-2-butanone	50[a]
	2-Propanone	6.2[a]
2-Phenyl-1-propene	2-Phenylpropanal	60[b]
1,1-Diphenylethene	2,2-Diphenylethanal	62.7[b]
	Benzophenone	3.4[b]
1,1,2,2-Tetraphenylethene	9,10-Diphenylphenanthrene	70[c]

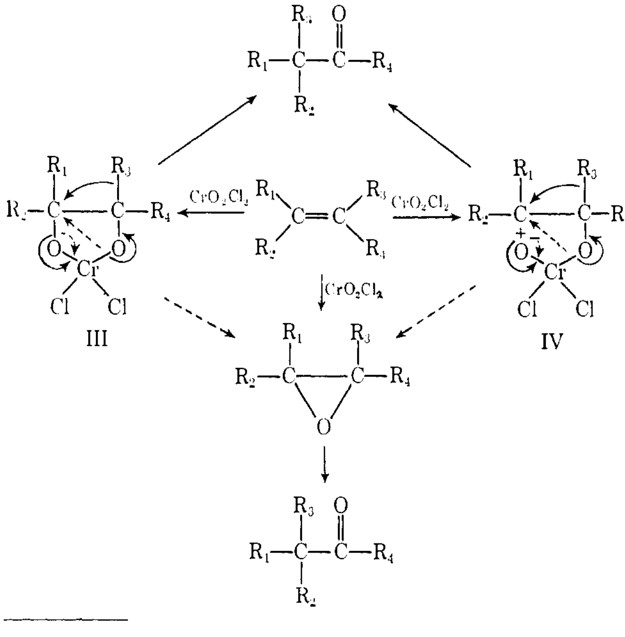
[a] See ref 7. [b] See ref 11. [c] A. L. Gatzke, R. A. Stairs, and D. G. M. Diaper, *Can. J. Chem.*, **46**, 3695 (1968).

obtain high yields of carbonyl products and to minimize undesirable secondary reactions (carbon–carbon double bond cleavage, chlorination),[7,11,13,14] the initially formed chromyl chloride–alkene adduct[15] is not isolated but hydrolyzed under reducing conditions.[13] Structures II–IV have been suggested as possible intermediates for the chromyl chloride oxidation of carbon–carbon double bonds.[6–9,11,14] Scheme I shows some of the possible reaction pathways. The question of the epoxide intermediate has not been resolved because epoxides are unstable to the hydrolytic conditions and rearrange to the corresponding carbonyl compounds.[7]

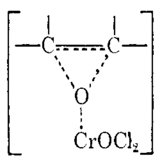


II

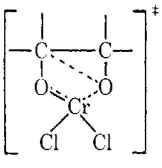
Scheme I



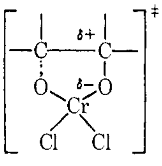
In spite of the many product studies, only two reports have appeared concerning the kinetics of the chromyl chloride oxidation of carbon–carbon double bonds.[1,18] Kinetic studies in our laboratories of the oxidation of cycloalkenes[18] suggest that the rate-determining step involves a three-membered ring activated complex similar to V or VI while rate data from the oxidation of styrenes[1] are consistent with the formulation of V, VI, VII, or VIII as the possible activated complex. Structure V is similar to the activated complexes formulated for the epoxidation of alkenes by peracids,[19] and for the oxidation of olefins by chromic acid.[20] Structure VI is similar to V except carbon–oxygen bond formation has occurred between the carbon of the carbon–carbon double bond and the oxygen of chromyl chloride prior to oxygen transfer. Structure IX, which could presumably represent a concerted *cis*-1,3-dipolar cycloaddition of chromyl chloride across the carbon–carbon double bond in the rate-determining step, is not consistent with the kinetic data for ring substituted and side-chain substituted styrenes.[1,10] Since the postulated transition states differ in the ring size of the cyclic activated complex, it seemed feasible to utilize the relative reactivity principles of Bartlett and Sargent (solvolyses),[21] of Awasthy and Roček



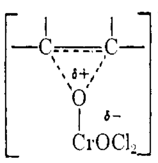
V



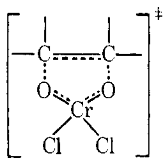
VI



VII



VIII



IX

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(13) Presumably the reducing agent (SO_2 or Zn dust) reduces any Cr(IV), Cr(V), or Cr(VI) (to Cr(III)) that might be formed during hydrolysis of the adduct. Zinc dust is the preferred reducing agent when aldehydes are formed.

(14) K. B. Wiberg, "Oxidation in Organic Chemistry," Part A, Academic Press, New York, N. Y., 1965.

(15) The chromyl chloride–organic adducts are generally hygroscopic and amorphous. Although the structure of the chromyl chloride–alkene adduct has not been fully elucidated, the cycloalkene[6,16] and styrene[9,17] adducts have a composition of 1 mol of chromyl chloride and 1 mol of unsaturate.

(16) R. A. Stairs, *Can. J. Chem.*, **38**, 2028 (1960).

(17) C. N. Rentea, M. Rentea, I. Necsoiu, and C. D. Nenitzescu, *Rev. Chem.* (Bucharest), **12**, 1495 (1967).

(18) F. Freeman and N. J. Yamachika, *Tetrahedron Lett.*, 3615 (1969).

(19) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).

(20) A. K. Awasthy and J. Roečk, *ibid.*, **91**, 991 (1969).

(21) P. D. Bartlett and G. D. Sargent, *J. Amer. Chem. Soc.*, **87**, 1297 (1965).

(chromic acid oxidation),[20] of Bingham, Meakins, and Whitham (epoxidation),[19,22] of Poutsma (chlorination),[23] of DuBois and Mouvier (bromination),[24] and of Skell and Garner (carbene addition)[25,26] in order to elucidate the nature of the activated complex in the chromyl chloride oxidation of alkenes. We have therefore obtained kinetic data for the chromyl chloride oxidation of fifteen substituted ethenes and compared the relative reactivities with bromination, chlorination, carbene addition, chromic acid oxidation, and *cis*-1,3-dipolar cycloaddition reactions in order to gain a clearer understanding of the rate-determining step. The kinetics, which were obtained spectrophotometrically in specially purified carbon tetrachloride, measure the rate of the electrophilic addition of chromyl chloride to the carbon–carbon double bond to give the chromyl chloride–alkene adduct (I).[15]

Experimental Section

Solutions of chromyl chloride and alkenes in specially purified carbon tetrachloride were prepared immediately before use.

Chromyl chloride (Alfa Inorganics, Inc.) was distilled and the middle fraction, bp 114.5–115.5°, used.

Alkenes. The following commercially available akenes were used: 1-pentene (technical grade),[27] 1-hexene,[28] 2,4,4-trimethyl-1-pentene,[28] *cis*- and *trans*-2-pentene,[28] 2,4,4-trimethyl-2-pentene,[28] 4,4-dimethyl-2-neopentyl-1-pentene,[28] 3,3-dimethyl-1-butene,[29] 2,3-dimethyl-2-butene,[28] and styrene.[27] The alkenes were refluxed for 2 hr with $LiAlH_4$[30] before distillation. All physical constants agreed with literature values.

Specially Purified Carbon Tetrachloride and Chloroform. This procedure is simpler and shorter than the previously described method.[1] A mixture of 1 l. of reagent or technical grade carbon tetrachloride and 3.8 g (0.025 mol) of chromyl chloride was allowed to stand at room temperature for at least 3 days in a dark closed container. The mixture was transferred to a large beaker, treated with 30 g of ice and 3.3 g (0.05 mol) of 90–95% technical grade zinc dust,[31] stirred 15 min, and then 30 g of ice, 30 g of water, and 25 ml of 6 *N* hydrochloric acid were added. After stirring 15–30 min (until disappearance of yellow color in CCl_4 layer), the mixture was separated and the organic layer washed once with water. The carbon tetrachloride was dried over $CaCl_2$ for 2 days, filtered, and the filtrate was distilled through a 4-ft bubble-chamber column at 65–67° to remove the $CCl_4 \cdot H_2O$ azeotrope (95.9% CCl_4 and 4.1% H_2O)[32] and at 76.8–77.0° to obtain pure carbon tetrachloride. The same procedure was used to purify chloroform (Mallinckrodt).

Apparatus. Owing to the rapid rate of oxidation, the kinetics were performed with a stopped-flow reactor[33,34] in a Beckman DU spectrophotometer. The spectrophotometer was connected *via* an energy recording adapter to a Bristol strip chart recorder (0.2-sec full-scale response and chart speeds to 120 in./min) or a Sargent Model SRLG recorder. Temperature was maintained with a Forma Model 2095-2 refrigerated and heated bath circulator.

Kinetic Method. All studies were performed under pseudo-first-order conditions (large excess of alkene), and the rates were determined by following the disappearance of chromyl chloride at 415, 430, and 440 mμ.[35,36] The pseudo-first-order rate constants (k_ψ) were calculated from the slopes of plots of $-\ln [(\log T_\infty/T)]$ *vs.* time.[1,33,37] T_∞ is the per cent transmission at a point just before the chromyl chloride–alkene adduct begins to form. The rate constants in the tables are the average of two or more determinations and were calculated on an IBM 1620 computer.[37]

Results

Effect of Dissolved Oxygen. The effect of dissolved oxygen was determined by degassing the solutions with oxygen-free nitrogen and then maintaining a nitrogen atmosphere above the solutions during the equilibration period (30 min) and during the kinetic experiment. No appreciable difference (always less than 8%) was observed when these pseudo-first-order rate constants (k_ψ) were compared with those obtained from otherwise identical nondegassed solutions.

Kinetic Data. The kinetic data for the addition of chromyl chloride to the carbon–carbon double bond of 2,4,4-trimethyl-1-pentene (X), to give the chromyl chloride–alkene adduct,[15] are summarized in Table II.

Table II. Kinetic Data for the Chromyl Chloride Oxidation of 2,4,4-Trimethyl-1-pentene at 10.0°

[2,4,4-Trimethyl-1-pentene] × 10^3 *M*	$[CrO_2Cl_2] \times 10^4$ *M*	k_ψ,[a] min^{-1}	k_2[b] × 10^{-2}, M^{-1} min^{-1}
4.00[c]	4.00	1.04	2.60
8.00[c]	4.00	1.89	2.36
16.0[c]	4.00	3.75	2.34
32.0[c]	4.00	7.44	2.32
40.0[c]	4.00	9.52	2.38
40.0[d]	2.00	10.5	2.62
40.0[e]	2.00	10.3	2.57
40.0[d]	4.00	10.4	2.61
40.0[e]	4.00	10.4	2.60
40.0[e]	6.00	11.0	2.74
40.0[d]	8.00	11.3	2.82
40.0[d]	10.00	11.3	2.84
40.0[d]	12.00	11.8	2.95

[a] Pseudo-first-order rate constant. [b] Second-order rate constant = k_ψ/[2,4,4-trimethyl-1-pentene]. [c] λ = 415 mμ. [d] λ = 440 mμ. [e] λ = 430 mμ.

The constancy of the values of the second-order rate constant ($k_2 = k_\psi$/[alkene]), at constant chromyl chloride concentration, over a tenfold range of 2,4,4-trimethyl-1-pentene (X) concentration indicates a first-order dependence on X. Further support for the first-order dependence on X is seen in a plot of k_ψ against 2,4,4-trimethyl-1-pentene (X) concentration (Figure 1) which gives a straight line that passes through the origin. At constant 2,4,4-trimethyl-1-pentene (X) concentration, the pseudo-first-order rate constant (k_ψ) did not alter appreciably over a sixfold range of chromyl chloride concentration when measured at 415, 430, and 440 mμ. These data are consistent with the rate law

$$\frac{-\mathrm{d}[CrO_2Cl_2]}{\mathrm{d}t} = k[\text{alkene}][CrO_2Cl_2] \qquad (2)$$

Thermodynamic Parameters. The rates of the chromyl chloride oxidation of six alkenes were determined at different temperatures. An Arrhenius plot

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(22) K. D. Bingham, G. D. Meakins, and G. H. Whitham, *Chem. Commun.*, 445 (1966).

(23) M. L. Poutsma, *J. Amer. Chem. Soc.*, 87, 4285 (1965).

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(26) W. von E. Doering and W. A. Henderson, *ibid.*, 80, 5274 (1958).

(27) Matheson Coleman & Bell.

(28) Aldrich Chemical Co., Inc.

(29) Sinclair Petrochemicals.

(30) Metal Hydrides, Inc.

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

(32) L. H. Horsley, *et al.*, "Azeotropic Data," No. 6, American Chemical Society, Washington, D. C., 1952.

(33) R. D. Geer, Ph.D. Thesis, University of Washington, Seattle, Wash., 1964.

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(36) A. Bartecki, *Rocz. Chem.*, 38, 1455 (1964).

(37) K. B. Wiberg, "Computer Programming for Chemists," W. A. Benjamin, Inc., New York, N. Y., 1965, p 168 ff.

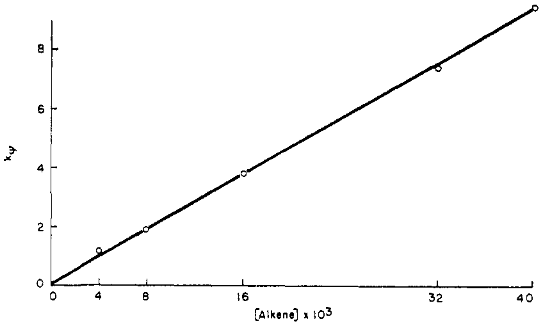

Figure 1. Effect of 2,4,4-trimethyl-1-pentene concentration on the pseudo-first-order rate constants (k_ψ) for the chromyl chloride oxidation of 2,4,4-trimethyl-1-pentene at 10.0°

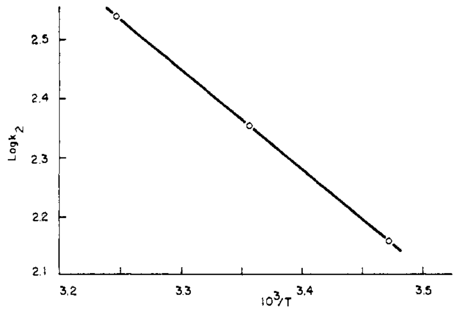

Figure 2. Effect of temperature on the chromyl chloride oxidation of 2,4,4-trimethyl-1-pentene. The conditions are [2,4,4-trimethyl-1-pentene] = 13.25 × 10^{-3} M, [CrO_2Cl_2] = 4.00 × 10^{-3} M.

of log k_2 *vs.* $1/T$ for the oxidation of X is shown in Figure 2, and the thermodynamic parameters for several alkenes are given in Table III.

Table III. Activation Parameters for the Chromyl Chloride Oxidation of Some Alkenes

Alkene	$\Delta F^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$-\Delta S^{\ddagger}$, eu
1-Hexene	17.5	6.2	40.7
3,3-Dimethyl-1-butene	17.7	7.0	38.5
2-Methyl-2-butene	14.8	7.2	27.4
2,3-Dimethyl-2-butene	13.2	5.4	27.9
2,4,4-Trimethyl-1-pentene	16.6	7.2	31.8
4,4-Dimethyl-2-neopentyl-1-pentene	17.2	6.5	36.8

Table IV. Effect of Solvents on the Rate of Chromyl Chloride Oxidation of 2,4,4-Trimethyl-1-pentene[a]

Solvent	k_2,[b] M^{-1} min^{-1}	μ[c]	ϵ[d]	E_T[e]	Z[f]	S[g]
CCl_4	240 ± 8	0.00	2.24	32.5	52.4	−0.245
$CHCl_3$	454 ± 11	1.15	4.81	39.2	63.2	−0.200

[a] [2,4,4-Trimethyl-1-pentene] = 4.0 × 10^{-3} M, [CrO_2Cl_2] = 4.0 × 10^{-4} M, λ = 415 mμ, T = 25.0° [b] $k_2 = k_\psi$/[alkene]. [c] Dipole moment: J. A. Riddick and E. Toops, Jr., "Techniques of Organic Chemistry," Vol. VII, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1965. [d] Dielectric constant (see footnote *c*). [e] K. Dimroth, C. Reichardt, T. Siepman, and F. Bohlmann, *Ann. Chem.*, **661**, 1 (1963). [f] E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3253 (1958). [g] S. Brownstein, *Can. J. Chem.*, **38**, 1590 (1960).

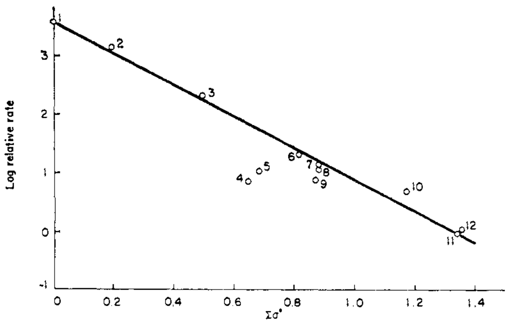

Figure 3. Correlation of log relative rate with the summation of Taft's polar substituent constant. The alkenes for the numbered points are as follows: 1, 2,3-dimethyl-2-butene; 2, 2,4,4-trimethyl-2-pentene; 3, 2-methyl-2-butene; 4, 4,4-dimethyl-2-neopentyl-1-pentene; 5, 2,3,3-trimethyl-1-butene; 6, 2,4,4-trimethyl-1-pentene; 7, 2-methyl-1-pentene; 8, *cis*-2-pentene; 9, *trans*-2-pentene; 10, 3,3-dimethyl-1-butene; 11, 1-hexane; 12, 1-pentene.

Effect of Solvents on Rates.[38] Table IV shows the effects of carbon tetrachloride and chloroform on the rate of chromyl chloride oxidation of X.

Relative Reactivities. The relative reactivities of fourteen alkenes, styrene, cyclohexene, cyclopentene, and norbornene toward chromyl chloride oxidation at 10.0° are summarized in Table V. A comparison of relative reactivities for reactions proceeding *via* three-membered ring activated complexes and five-membered ring activated complexes are also given in Table V.

Linear Free Energy Relationships. Assuming simple additivity of substituent effects[39] and neglecting interaction terms,[40] a linear correlation with log relative rates *vs.* Taft's[39] inductive σ^* substituent constants were obtained (Figure 3). Excluding 4,4-dimethyl-2-neopentyl-1-pentene (XI) and 2,3,3-trimethyl-1-butene (XIII), statistical treatment of the data[41] gave ρ^* −2.63, a correlation coefficient (r) of 0.991, and a standard deviation (s) of 0.171.

Correlation (Table VI)[42] of the kinetic data from seven alkenes (XII–XVIII) with the extended form of the Hammett equation (3) gave the results shown in

$$Q_x = \alpha\sum\sigma_{I,X} + \beta\sum\sigma_{R,X} + h \tag{3}$$

Table VII as set 1.[43,44] Correlation with the two-parameter equation (4) employing Taft's inductive σ^*

$$Q_x = \alpha\sum\sigma_{I,X} + \beta\sum E_{s,x} + h \tag{4}$$

constants and steric substituent constants (E_s) gave the results in set 2 (Table VII),[39,44] and attempted correlation with three independent variables (eq 5) gave the

$$Q_x = \alpha\sum\sigma_{I,X} + \beta\sum\sigma_{R,X} + \gamma\sum E_{s,x} + h \tag{5}$$

results in set 3 (Table VII).[42,44] The results of the correlation between inductive effects and steric effects, according to eq 6, are given as set 4 in Table VII.

$$Q_x = \alpha\sum\sigma_{I,X} + \beta\sum E_{s,x} + h \tag{6}$$

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(38) Since chromyl chloride reacts with most organic compounds, very few solvents are available for rate studies. However, a variety of solvents are currently being evaluated.

(39) R. W. Taft, Jr. in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 556.

(40) S. I. Miller, *J. Amer. Chem. Soc.*, **81**, 101 (1959).

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Table V. Relative Reactivities of Some Alkene in Various Addition Reactions

Alkene	Chromyl chloride oxidation[a]	Chromic acid oxidation[b]	Epoxidation[c]	Br_2 addition[d,e]	Cl_2 addition[f,g]	:CBr_2 addition[h]	Picryl azide addition[i,j]	Benzonitrile oxide addition[k]
1-Pentene	1.22	0.76	0.88	1.05			1.00	
1-Hexene	1.00	1.00	1.00	1.00		1.00		1.00
1-Octene	0.77		1.02				0.66	
1-Decene	0.88		0.96					
2-Methyl-1-pentene	8.00							
3,3-Dimethyl-1-butene	5.36	0.69			0.023			
4,4-Dimethyl-2-neopentyl-1-pentene	7.54							
2,3,3-Trimethyl-1-butene	10.5							
2,4,4-Trimethyl-1-pentene	23.6							
cis-2-Pentene	14.8			63.3				
trans-2-Pentene	15.1	2.5						
2-Methyl-2-butene	202	31.3			220	45.7		
2,3-Dimethyl-2-butene	3910	160	Very rapid	14,000	8600	50		
2,4,4-Trimethyl-2-pentene	1380	11.0		413				
Cyclopentene	4.9[g,l,m]	31.7	37.8	38[n,o]		7.1	10.6	0.4
Cyclohexene	1.0[g,l,m]	24.6	26.3	28[n,o]	1.00	5.7	0.25	0.02
Norbornene	312[g,l,m]	135					2,000	37.3
Styrene	366	56.8	2.3			5.7	1.03	3.6

[a] This work. [b] See ref 20. [c] D. Swern, *Chem. Rev.*, **45**, 49 (1949). [d] See ref 23. [e] Measured in methanol–0.2 *N* NaBr. [f] See ref 22. [g] Relative rates compared with cyclohexene. [h] See ref 24. [i] A. S. Bailey and J. E. White, *J. Chem. Soc.*, *B*, 819 (1966). [j] Relative rates compared to 1-pentene. [k] R. Huisgen, R. Graskey, and J. Sauer, "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, London, 1964, p 826. [l] F. Freeman and K. W. Arledge, unpublished results, 1969. [m] See ref 18. [n] P. W. Robertson, J. K. Heyes, and B. E. Swedlund, *J. Chem. Soc.*, 1014 (1952). [o] Measured in HOAc.

Table VI. Correlation of the Rates of Chromyl Chloride Oxidation of Some Alkenes with Various Substituent Constants

Alkene	k_2, M^{-1} min^{-1}	$\Sigma\sigma_I$[a]	$\Sigma\sigma_R$[a]	$\Sigma\sigma^*$	ΣE_s[b]
$CH_2{=}C(CH_3)(neo\text{-}C_5H_{11})$ (X)	104			0.815	0.74
$CH_2{=}C(neo\text{-}C_5H_{11})_2$ (XI)	33.3			0.650	−1.00
$(CH_3)_2C{=}C(CH_3)_2$ (XII)	17250	−0.184	−0.408	0.00	0.00
$CH_2{=}C(CH_3)(t\text{-}C_4H_9)$ (XIII)	46.3	−0.120	−0.180	0.68	0.94
cis-$CH_3CH{=}CHCH_3$ (XIV)	66.4	−0.092	−0.204	0.88	2.48
trans-$CH_3CH{=}CHCH_3$ (XV)	61.0	−0.092	−0.204	0.88	2.48
$CH_3CH{=}C(CH_3)_2$ (XVI)	890	−0.138	−0.306	0.49	1.24
$CH_2{=}CH(t\text{-}C_4H_9)$ (XVII)	23.6	−0.074	−0.078	1.17	−2.18
$(CH_3)_2C{=}CH(t\text{-}C_4H_9)$ (XVIII)	6060	−0.166	−0.282	0.19	−0.30
$CH_2{=}CH(n\text{-}C_3H_7)$ (XIX)	5.40			1.37	3.36
$CH_2{=}CH(n\text{-}C_4H_9)$ (XX)	4.41			1.34	3.33
$CH_2{=}CH(n\text{-}C_6H_{13})$ (XXI)	3.41				
$CH_2{=}CH(n\text{-}C_8H_{17})$ (XXII)	3.89				3.39
$CH_2{=}C(CH_3)(n\text{-}C_3H_7)$ (XXIII)	35.3			0.865	2.12

[a] See ref 42. [b] See ref 39.

Table VII. Results of Correlations

Set	α	β	γ	h	R[a]	F[b]	r[c]	s_{est}[d]	s_α[d]	s_β[d]	s_γ[d]	s_h[d]	t_α[e]	t_β[e]	t_γ[e]	t_h[e]
1	−19.4	−3.04		−1.25	0.963	25.7	0.900[f]	0.374	8.56	3.33		0.508	−2.27	−0.912		−2.45
2	−2.55	0.017		3.33	0.945	37.5	0.449	0.402	0.325	0.078		0.255	−7.83	0.215		13.0
3	−10.1	−6.76	−0.152	0.877	0.977	20.5	0.900[f] 0.116[g] −0.190[h]	0.347	10.7	4.22	0.118	0.551	−0.942	−1.60	−1.29	−1.59
4	−26.3	−0.023		−1.37	0.956	21.2	0.116[g]	0.409	4.09	0.110		0.541	−6.44	0.230		−2.53

[a] Multiple correlation coefficient. [b] F test for significance of regression. [c] Partial correlation coefficient of independent variable on each other. [d] Standard errors of estimate for α, β, γ, h. [e] "Student t" tests for significance of α, β, γ, h. [f] Partial correlation coefficient of σ_I on σ_R. [g] Partial correlation coefficient of σ_I on E_s. [h] Partial correlation coefficient of σ_R on E_s.

Discussion

The fact that alkenes react with chromyl chloride to give rearranged products demonstrates that a carbonium ion intermediate or a partially positively charged species must be involved in the reaction prior to or after the rate-determining step. Also, the kinetic data establish that the electrophilic attack of chromyl chloride at the carbon–carbon double bond of alkenes, to give the chromyl chloride–alkene adduct, is first order with respect both to oxidant and to the reductant (eq 2). This is consistent with a rate-determining step involving the components of alkene and chromyl chloride.

It is clear from Table V that the rate of oxidation is markedly increased by the electron-releasing influence of alkyl substituents at the carbon–carbon double bond. Indeed, 2,3-dimethyl-2-butene (XII) reacts 10.7 times faster than styrene (XXIII).[45] The differences (though small) in reactivity between *cis*- and *trans*-2-pentene (XIV, XV) and between cyclopentene (XXIV) and cyclohexene (XXV) are also noteworthy.

The large values of α in Table VII show the strong inductive influence on the reaction, and the results obtained with sets 1 and 3 show that γ is significant for the correlation of σ_I and σ_R. Thus no separation of σ_I and σ_R can be achieved for the substituents studied. The results obtained for sets 2 and 4 show clearly that the oxidation is rather insensitive to steric factors.

Although more studies on solvent effects are required, it is seen from the preliminary data that the rate of oxidation increases with an increase in solvent polarity (Table IV). This is consistent with a mechanism involving charge development in the rate-determining step.

The close mechanistic parallel between the chromyl chloride oxidation of alkenes and olefinic reactions with bromine, chlorine, chromic acid, and peracids is shown by the relative rates of reactions in Table V. It is seen from inspection of the limited data in Table V that there is little variation of rate with XII and XVI for dibromocarbene addition. Also, the relatively small differences in the reactivities of XXIV and XXV appear to be general for reagents (bromine, chlorine, chromic acid, peracids, carbenes) that presumably react with carbon–carbon double bonds *via* three-membered ring activated complexes.[20]

Comparisons of the relative rates indicate that the activated complex for the chromyl chloride oxidation of alkenes involves partial bonding of the chromyl chloride molecule with one or both termini of the unsaturated system with little development of positive charge on the more highly substituted carbon. Thus the activated complex for the rate-limiting step probably resembles V, VI, VII, or VIII. A concerted *cis*-1,3-cycloaddition of chromyl chloride to the alkene to give the symmetrical five-center activated complex IX seems unlikely because of the negative value of ρ ($\rho^* = -2.63$), the dramatic increase in rate with increasing alkyl substitution, and the insensitivity of rates to steric factors.[48] Steric factors are especially important in other addition reactions of XI since it is not readily attacked by hot permanganate,[49] by chromic acid,[50] and does not add bromine.[51]

Although the rate data do not clearly distinguish among structures V–VIII, it is probable that the rate-limiting activated complex of formation of the chromyl chloride–alkene adduct closely resembles V. The relative rate data and comparison of relative rates with bromine and chlorine additions, chromic acid oxidation, and epoxidation are compatible with a partly bridged three-membered ring-activated complex (V). Such a partially bridged activated complex can support an increasing positive charge as alkyl substitution increases about the carbon–carbon double bond. That is, bond formation is greater between the less substituted carbon of the carbon–carbon double bond and the oxygen of chromyl chloride than between the more substituted carbon of the carbon–carbon double bond. Presumably, as bonding increases between oxygen and the more substituted carbon, the oxygen–chromium bond is breaking.

An attempt has been made to correlate eq 3 with a series of electrophilic–addition reactions to the carbon–carbon double bond.[52] It was postulated in cases where the localized effect predominates ($\alpha > \beta$) that the reaction proceeds *via* the formation of a bridged activated complex. Structures V–VIII are consistent with this argument. Furthermore, V–VIII would require a high state of order in the rate-determining step which is consistent with the observed large negative values for the entropies of activation. Also, the observed ρ^* value of -2.63 is smaller than those generally observed for reactions involving fully developed carbonium ions in the transition state.[1]

While it is difficult to formulate a detailed mechanism for the chromyl chloride oxidation of alkenes and styrenes,[1] it is clear that both reactions are characterized by rather low energies of activation and quite negative entropies of activation. Also, Table III shows that changes in $\Delta F^{\ddagger}$ with structure are not the result of compensating but rather random changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.[1,10]

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