the ceric sulfate oxidation of cyclopropanols and cyclopropanone hemiacetal.[31]

Conclusion

The results of this study confirm that cyclobutanol is uniquely reactive toward one-electron oxidants and reacts with carbon–carbon bond cleavage involving the formation of a free-radical intermediate.

Acknowledgments. We should like to thank Dr. Michael P. Doyle, Mr. William E. Delaney, and Mr. Robert Arnold, who carried out the initial experiments and were the first to notice the unusually high reactivity of cyclobutanol toward cerium ammonium nitrate. We are particularly indebted to Professor Doyle for his help in the preparation of this paper and the many useful suggestions for its improvement.

---

(31) This interpretation is based on the assumption that cyclopropanol and its derivatives are considerably more reactive to cerium(IV) than even the highly reactive cyclobutanol. While no rate data are reported, the assumption seems at least plausible.

Chromyl Chloride Oxidations. VI. Nature of the Activated Complex in the Electrophilic Addition to Styrenes[1,2]

Fillmore Freeman* and Nira J. Yamachika[3]

Contribution from the Department of Chemistry, California State College, Long Beach, California 90801. Received April 15, 1971

Abstract: The kinetics of the rapid chromyl chloride addition to (oxidation of) styrene (**4**) and substituted styrenes, to give the 1:1 chromyl chloride–styrene adducts, have been measured using a spectrophotometric stopped flow system. The rates of addition are increased by electron releasing groups on the benzene ring. α-Methylstyrene is more reactive than *cis*-β-methylstyrene. *cis*-β-Methylstyrene is oxidized at a slower rate than the corresponding trans isomer while *cis*-stilbene reacts almost twice as fast as *trans*-stilbene. 1,1-Diphenylethene is almost twice as reactive as α-methylstyrene and approximately 13 times as reactive as styrene (**4**). The kinetic data suggest an unsymmetrically charged benzylic type carbonium ion like activated complex in the rate-determining step for the chromyl chloride addition to styrenes. The relative rates of oxidation of **4** in carbon disulfide, carbon tetrachloride, chloroform, and CH_2Cl_2 are 1.0:1.1:1.7:5.3. A negligible secondary deuterium kinetic isotope effect of 0.98 is observed in the oxidation of α-deuteriostyrene, and an inverse secondary deuterium kinetic isotope effect ($k_H/k_D = 0.88$) is obtained in the oxidation of β,β-dideuteriostyrene. Large negative entropies of activation ($\Delta S^{\ddagger} = -23.8$ to -42.4 eu) and low enthalpies of activation ($\Delta H^{\ddagger} = 2.0$–$9.0$ kcal/mol) are characteristic of the oxidations. The kinetic data, including the previously observed ρ^+ of -1.99, suggest a rate-determining step involving a partially positive charged benzylic carbon atom in a cyclic epoxide like three-membered ring activated complex or in a partly bridged resonance-stabilized five-membered ring-activated complex. Comparisons of product yields from the chromyl chloride, chromyl acetate, and chromic acid oxidations of unsaturated hydrocarbons suggest that chromyl chloride is the preferred oxidant for a one-step high-yield conversion of 2,2-disubstituted alkenes to aldehydes and ketones. A comparison of the postulated activated complexes for the oxidation of carbon–carbon double bonds by chromic acid, chromyl acetate, and chromyl chloride is also presented.

The chromyl chloride oxidation of unsaturated hydrocarbons is of particular interest because preliminary studies indicate that it might become the most synthetically useful of the readily available and versatile chromium(VI) oxidizing agents for the oxidation of carbon–carbon double bonds to aldehydes and ketones. Oxidation of carbon–carbon double bonds with chromyl acetate and chromic acid can lead to formation of a large variety of compounds, including epoxides, glycols, aldehydes, ketones, acids, and cleavage products. In contrast, chromyl chloride oxidizes unsaturated hydrocarbons to aldehydes and ketones in good to excellent yields without serious side reactions. Table I shows the products from the oxidation of a variety of unsaturated hydrocarbons with chromyl chloride, chromyl acetate, and chromic acid.

Styrenes, which have been postulated as intermediates in the chromyl chloride oxidation of aryl alkanes (Étard reaction),[4,5] react with chromyl chloride to give adducts consisting of one part oxidant and one part reductant.[6,7] Hydrolyses of these adducts under reducing conditions give aldehydes and ketones which result from structural rearrangements (Scheme I).[4,8,9] The yields range from fair to excellent.[1,4,5] Kinetic studies of the electrophilic addition of chromyl chloride to carbon–carbon double bonds have shown that there are several reasonable mechanistic pathways available for reaction. The first kinetic study of the chromyl chloride oxidation of styrene[9] revealed that the reaction is first order in

---

* Address correspondence to this author at: Physical Organic Chemistry Laboratory, University of Paris VII, Paris, 5^e, France.

(1) Previous paper in series: F. Freeman, P. D. McCart, and N. J. Yamachika, *J. Amer. Chem. Soc.*, 92, 4621 (1970).

(2) Presented in part at the Pacific Conference on Chemistry and Spectroscopy, San Francisco, Calif., Oct 8, 1970.

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

(4) K. B. Wiberg, B. Marshall, and G. Foster, *Tetrahedron Lett.*, 345 (1962).

(5) I. Necsoiu, A. Ghenciulescu, M. Rentea, C. N. Rentea, and C. D. Nenitzescu, *Rev. Roum. Chim.*, 12, 1503 (1967).

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

(7) Table I, footnote *q*.

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

(9) F. Freeman and N. J. Yamachika, *J. Amer. Chem. Soc.*, 92, 3730 (1970).

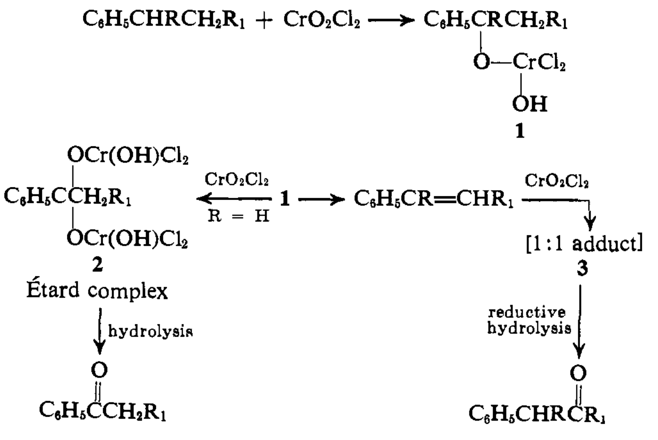
Table I. Products from the Oxidation of Unsaturated Hydrocarbons by Some Chromium(VI) Oxidants

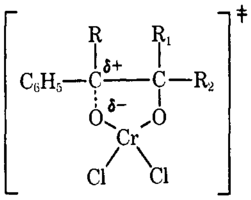
		Products (% yield)	
Unsaturate	CrO_2Cl_2	$CrO_2(OAc)_2$[a]	H_2CrO_4[b]
2,3-Dimethyl-2-butene	3,3-Dimethyl-2-butanone (50)[c] 2-Propanone (6)[c]	2,3-Dimethyl-2-butenal 3,3-Dimethyl-2-butanone $\}$ (3)[d,e] 2,3-Dimethyl-1,2-epoxybutane (9)[d,e]	3,3-Dimethyl-2-butanone (11)[e,f] 2-Propanone (6)[e,f] 2,2-Dimethylpropanoic acid (trace)[e,f]
2,4,4-Trimethyl-1-pentene	2,4,4-Trimethylpentanal (75.8)[c]	2,4,4-Trimethylpentanal (low)[g] 4,4-Dimethyl-2-pentanone (low)[g] 2,4,4-Trimethylpentane-1,2-diol (15)[g] 2,4,4-Trimethyl-1,2-epoxypentane (21)[g]	4,4-Dimethyl-2-pentanone (low)[g,h] 2,4,4-Trimethylpentanoic acid (low)[g,h]
4,4-Dimethyl-2-neopentyl-1-pentene	4,4-Dimethyl-2-neopentylbutanal (80.8)[c]	4,4-Dimethyl-2-neopentyl-1,2-epoxypentane (low)[i] 3,3-Dimethyl-2-neopentylbutanoic acid (low)[i]	3,3-Dimethyl-2-neopentylbutanoic acid (24.7)[i–k]
Camphene	Camphenilanaldehyde[l–n]	Camphene oxide (12)[o]	Camphor[o,p]
Styrene	Phenylethanal (76.5)[q] Phenylmethanal (21.1)[q] Phenylethanone (2.4)[q]		
2-Phenyl-1-propene	2-Phenylpropanal (60)[r]		
1,1-Diphenylethene	2,2-Diphenylethanal (62.7)[r] Diphenyl ketone (3.4)[r]	*s*, *t*	*t*, *u*
1,1,2,2-Tetraphenylethene	9,10-Diphenylphenanthrene (70)[v]	1,1,2,2-Tetraphenyl-1,2-epoxyethane (20)[w] Diphenyl ketone (5)[w] Benzopinacol carbonate (60)[w]	1,1,2,2-Tetraphenyl-1,2-epoxyethane (70)[w,x] Diphenyl ketone (16)[w,x]

[a] Chromium trioxide in acetic anhydride. [b] Chromium trioxide in aqueous sulfuric acid. [c] F. Freeman, P. J. Cameron, and R. H. DuBois, *J. Org. Chem.*, **33**, 3970 (1968); F. Freeman, R. H. Dubois, and T. G. McLaughlin, *Org. Syn.*, **51**, 4 (1971). [d] Per cent conversion.[e] [e] W. J. Hickinbottom, E. R. Hogg, D. Peters, and D. G. M. Wood, *J. Chem. Soc.*, 4400 (1954). [f] A. Butlerow, *J. Russ. Phys. Chem. Soc.*, **12,** 1482 (1879). [g] A. Byers and W. J. Hickenbottom, *J. Chem. Soc.*, 1334 (1948). [h] A technical diisobutylene mixture of 80% 2,4,4-trimethyl-1-pentene and 20% 2,4,4-trimethyl-2-pentene was used. [i] W. J. Hickinbottom and D. G. M. Wood, *J. Chem. Soc.*, 1600 (1951). See also, K. B. Wiberg, "Oxidation in Organic Chemistry," Part A, Academic Press, New York, N. Y., 1965, p 13. [j] F. C. Whitmore and J. D. Surmatis, *J. Amer. Chem. Soc.*, **63**, 2200 (1941). [k] P. D. Bartlett, G. L. Fraser, and R. B. Woodward, *ibid.*, **63**, 496 (1941). [l] A. Étard, *Ann. Chem. Phys.*, **22,** 218 (1881). [m] J. Bredt and W. Jagelki, *Ann. Chem.*, **30**, 112 (1900). [n] The reactants and products probably should be reinvestigated. [o] W. J. Hickinbottom and D. G. M. Wood, *J. Chem. Soc.*, 1906 (1953). [p] Presumably camphene is isomerized and hydrated to isoborneol in the acidic reaction medium. Subsequent oxidation of isoborneol would be expected to give camphor. [q] C. N. Rentea, M. Rentea, I. Necsoiu, and C. D. Nenitzescu, *Rev. Roum. Chem.*, **12**, 1495 (1967). [r] See ref 8. [s] Oxidation of 1,1-diarylethylenes generally gives the corresponding epoxide.[t] [t] W. J. Hickinbottom and G. E. M. Moussa, *J. Chem. Soc.*, 4195 (1957); G. E. Moussa, *J. Appl. Chem.* (*London*), **12,** 385 (1962). [u] Oxidation of 1,1-diarylethylenes gave only cleavage products and no epoxides. [v] A. L. Gatzke, R. A. Stairs, and D. G. M. Diaper, *Can. J. Chem.*, **46**, 3695 (1968). [w] W. A. Mosher, F. W. Steffgen, and P. T. Lansbury, *J. Org. Chem.*, **26**, 670 (1961). [x] Glacial acetic acid solvent: W. Bockemuller and R. Janssen, *Justus Liebigs Ann. Chem.*, **542**, 166 (1939); A. Behr, *Chem. Ber.*, **5**, 277 (1872).

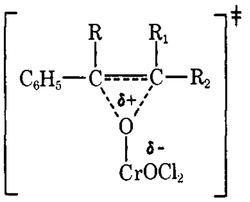
styrene (**4**) and first order in chromyl chloride. The kinetic data are consistent with the formulation of **5**, **6**, or **7** as the possible rate-limiting activated complex of formation of the chromyl chloride–styrene adduct (**3**).

Scheme I

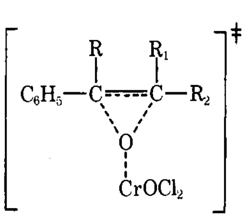




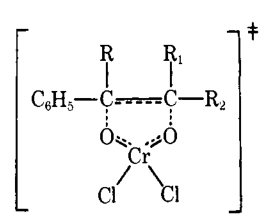
5



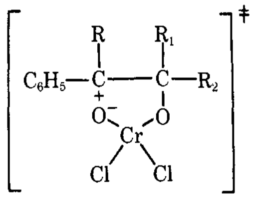
6



7



8

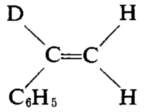


9

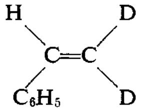
Structure **8**, which could represent the activated complex for a rate-determining step for a concerted cis 1,3-cycloaddition of chromyl chloride to the carbon–carbon double bond of **4**, was considered an unlikely possibility due to the magnitude of the observed ρ value (ρ^+ = 1.99).[10–14] However, concerted mechanisms of cycloaddition with charge unbalance in the transition state have been postulated.[15,16] On the other hand, since ρ^+ values of -3 to -5 are observed in reactions involving a fairly large degree of carbonium ion character in the activated complex, the relatively low ρ^+ value of -1.99 mitigates against a fully developed positive charge on the benzylic carbon atom which could resemble **9**.[9]

Spectrophotometric stopped flow kinetic studies of the chromyl chloride oxidation of alkenes are consistent with a rate-determining step involving **6**.[1] Preliminary kinetic data from cyclopentene and cyclohexene oxidations also suggest that the rate-limiting step involves a three-membered ring activated complex resembling **6** or **7**.[17,18] In contrast, preliminary studies with norbornene, and comparison of relative rate data, imply that the activated complex for the oxidation of the bicyclic system might show a close resemblance to **5**, **6**, or **9**.[17,18]

In order to obtain more data concerning the postulated activated complexes for the chromyl chloride oxidation of (addition to) styrenes, we have investigated the kinetics of the oxidation of ring- and side-chain substituted styrenes, α-deuteriostyrene (**10**), and β,β-dideuteriostyrene (**11**) using spectrophotometric stopped-flow techniques.[1,19,20] The kinetics measure the rate of electrophilic addition of chromyl chloride to the carbon–carbon double bond to give the 1:1 chromyl chloride–styrene adduct **3**.[5,9]



10



11

Experimental Section

Styrenes. Most of the styrenes were obtained commercially: styrene,[21] α-methylstyrene,[22] *cis*-β-methylstyrene (98%),[23] *trans*-β-methylstyrene,[22] *cis*-stilbene,[22] *trans*-stilbene,[24] 1,1-diphenylethene,[22] *p*-C_5H_5, *p*-Br, and *p*-CH_3 styrene.[24] *p*-Phenylstyrene (technical) was recrystallized several times from dilute ethyl alcohol. Specially purified solvents,[1] chromyl chloride,[25] and the liquid styrenes were distilled immediately before use. The melting points and boiling points of all reagents agreed well with literature values.

1-Phenylethanol-*1-d* (12). To a solution of 2.0 g (0.048 mol) of 99% $LiAlD_4$ (Isotopes, Inc.) in 380 ml of anhydrous diethyl ether contained in a 1-l. three-necked round-bottomed flask equipped with a reflux condenser, a stirrer, a dropping funnel, and a drying tube was added 20 g (0.166 mol) of freshly distilled acetophenone[22] in 80 ml of anhydrous diethyl ether in a dropwise manner. After the solution had been stirred for 1 hr, the complex was destroyed with 16 ml of distilled water. The mixture was poured into 300 ml of 1 *N* HCl and stirred until no solid remained. The layers were separated, the aqueous portion was extracted four times with 50-ml portions of ether, and the combined organic portions were dried over anhydrous $MgSO_4$. After the drying agent was removed by filtration and the ether by distillation, the product was distilled to give a 90% yield of 1-phenylethanol-*1-d* (**12**), bp 91–93° (5 mm) [lit.[26,27] 65° (2 mm); 60–80° (1 mm)]. Vpc analysis on a 10 ft × 1/4 in. 10% Apiezon L on Chromosorb W column at 155° indicated trace amounts of styrene and acetophenone. The pmr spectrum confirmed the label at the α position.

α-Deuteriostyrene (10). Dehydration of **12** with a trace of *p*-toluenesulfonic acid as catalyst and a trace of picric acid as polymerization inhibitor[26] gave **10**: bp 76.5–77.0° (60 mm); $n^{22}\mathrm{D}$ 1.5458 (lit.[28] bp 55° (28 mm)); $n^{27}\mathrm{D}$ 1.5425). No detectable absorption by α-hydrogen could be seen in the 60-MHz pmr spectrum. Vpc analysis on a 10 ft × 1/4 in. 10% Apiezon L on Chromosorb W column showed only one peak. The styrene was stabilized with a trace of 4-*tert*-butylcatechol.

2-Phenylethanol-*1,1-d₂* (13). To a three-necked round-bottomed flask equipped with a stirrer, dropping funnel, and reflux condenser (with $CaCl_2$ drying tube) were added 2 g (0.048 mol) of 99% $LiAlD_4$ (E. Merck AG) and 100 ml of dry diethyl ether. A solution of 15.7 g (0.096 mol) of freshly distilled ethyl phenylacetate (Eastman) and 100 ml of dry ether was added at a rate to maintain gentle reflux over a 35-min period. After addition the reaction mixture was heated at gentle reflux for 1 hr, cooled, and treated with 20 ml of 30% Rochelle salts solution. The ether layer was separated, dried over anhydrous Na_2SO_4, and distilled to give a 91% yield of 2-phenylethanol-*1-d₂* (**13**): bp 75.8–76.0° (1 mm); $n^{25}\mathrm{D}$ 1.5219 [lit.[28] bp 103° (12 mm), $n^{29}\mathrm{D}$ 1.5279].

β,β-Dideuteriostyrene (11). Dehydration of **13** with potassium hydroxide[29] gave **11**, bp 28.8° (1 mm) [lit.[30] 54° (31 mm)]. The pmr spectrum did not show absorption for β protons.

Solvent Purification. Carbon tetrachloride, chloroform (Mallinckrodt), methylene chloride,[21] carbon disulfide (Mallinckrodt), benzene (Baker), and chlorobenzene (Eastman) were purified as previously described.[1]

Kinetic Measurements. The very rapid rates of oxidation were studied under pseudo-first-order conditions *via* the previously described[1,19,20,31,33] spectrophotometric stopped-flow technique. The pseudo-first-order rate constants (k_ψ) were obtained from the slopes of plots of $-\ln [\log (T_\infty/T)]$ against time, and were calculated on an IBM 1620 computer.[34] T_∞ is the per cent transmission at a point just before the chromyl chloride–styrene adduct begins to form (after at least two half-lives). Each rate constant is the average of at least two determinations.

Apparatus. All connections in the stopped-flow reactor were Pyrex glass and Teflon since methylene chloride and chloroform appeared to react and/or dissolve the usual tygon connections.

Results

Effect of Oxygen and Light on Rates. The rates of oxidation of styrenes in carbon tetrachloride solution were not appreciably affected by light or oxygen.[1] Essentially the same pseudo-first-order rate constants (k_ψ) were obtained in the light, in the dark, and when the solutions were degassed by purging with oxygen-free nitrogen and maintaining the system in an inert (nitrogen) atmosphere during temperature equilibrations and rate measurements.

Thermodynamic Parameters and Relative Rates. The relative rates of the electrophilic addition of chromyl

---

(10) Cis cycloaddition mechanisms involving permanganate ion oxidations,[11-13] and cis 1,3-dipolar cycloadditons to carbon–carbon double bonds[14] are characterized by values close to zero.

(11) F. Freeman and A. Yeramyan, *J. Org. Chem.*, **35**, 2061 (1970).

(12) F. Freeman and D. K. Lin, *ibid.*, **36**, 1335 (1971).

(13) K. B. Wiberg and R. D. Geer, *J. Amer. Chem. Soc.*, **88**, 5827 (1966).

(14) R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, London, 1964, p 644.

(15) P. Beltrame and C. Vintani, *J. Chem. Soc. B*, 873 (1970).

(16) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 633 (1963).

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

(18) F. Freeman and K. W. Arledge, unpublished results, 1969.

(19) K. B. Wiberg and R. D. Geer, *J. Amer. Chem. Soc.*, **87**, 5202 (1965).

(20) F. Freeman, A. Yeramyan, and F. Young, *J. Org. Chem.*, **34**, 2438 (1969).

(21) Matheson Coleman and Bell.

(22) Aldrich Chemical Co., Inc.

(23) Chemical Samples Co., Columbus, Ohio.

(24) K & K Laboratories, Inc.

(25) Alfa Inorganics.

(26) J. B. Lambert and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 3891 (1965).

(27) M. Buza and E. I. Snyder, *ibid.*, **88**, 1161 (1966).

(28) K. R. Kopecky and S. Evani, *Can. J. Chem.*, **47**, 4049 (1969).

(29) S. Sabetay, *Bull. Soc. Chem. Fr.*, **45**, 69 (1929).

(30) G. S. Hammond and K. R. Kipecky, *J. Polym. Sci.*, **60**, (1962).

(31) Chromyl chloride has a uv max at 290 mμ and a visible max at 415 mμ.[32,33]

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

(33) O. H. Wheeler, *Can. J. Chem.*, **38**, 2137 (1960).

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

chloride to **4**, to three ring-substituted styrenes, and to nine side-chain substituted styrenes are given in Table II. Figure 1 shows the effect of temperature on the chromyl chloride oxidation of **4**.

Table II. Relative Rates of Oxidation and Thermodynamic Parameters for Some Styrenes

Styrene	k_2, M^{-1} sec^{-1}, 10°	Rel rates		$\Delta H^{\ddagger}$, kcal/mol	$-\Delta S^{\ddagger}$, eu
		10°	20°		
Styrene	29.3	1.0	1.0	8.1	23.8
4-Phenylstyrene	98.5^a	2.7^a		2.0	42.4
4-Bromostyrene	16.5^a	0.45^a		4.3	37.9
4-Methylstyrene	150.6^a	4.1^a		4.6	32.6
α-Methylstyrene	193.8^b	7.3^b		5.8	29.9
cis-β-Methylstyrene	50.7^b	1.9^a	1.9^b	8.0	20.1
trans-β-Methylstyrene	222.6^b	8.3		5.9	29.3
cis-Stilbene	8.41	0.29	0.32	8.96	37.9
trans-Stilbene	4.69	0.16	0.17	8.17	26.5
1,1-Diphenylethene	359.6	12.8		3.3	35.3
Triphenylethene	11.8	0.40	0.44	8.6	23.3
Tetraphenylethene	0.32	0.01			
3-Phenylpropene	0.29	0.01			

[a] Rates compared at 15°. [b] Rates compared at 5°.

Effect of Solvents on Rates of Oxidation. Table III shows the effects of carbon disulfide, carbon tetrachloride, chloroform, and methylene chloride on the rate of chromyl chloride oxidation of **4**.

Table III. Effect of Solvents on the Rate of Chromyl Chloride Oxidation of Styrene[a]

Solvent	k_2,[b] M^{-1} sec^{-1}	Rel rate	$\mu^{c,d}$	$\epsilon^{d,e}$	$E_T{}^f$	Z^g	S^h
CS_2	24.9	1.0	0.00	2.64	32.6		−0.240
CCl_4	26.7	1.1	0.00	2.24	32.5	52.4	−0.245
$CHCl_3$	43.4	1.7	1.15	4.81	39.2	63.2	−0.200
CH_2Cl_2	132.9	5.3	1.55	9.08	41.1	64.2	−0.189

[a] [Styrene] = 4.0×10^{-3} *M*, [CrO_2Cl_2] = 4.0×10^{-4} *M*, λ = 415 mμ, T = 5.0°. [b] Second-order rate constant = k_ψ/[styrene]. [c] Dipole moment. [d] J. A. Riddick and E. Toops, Jr., "Techniques of Organic Chemistry," Vol. VII, A. Weissberger, Ed., Interscience, New York, N. Y., 1965. [e] Dielectric constant. [f] K. Dimroth, C. Reichardt, T. Siepman, and F. Bohlmann, *Justus Liebigs Ann. Chem.*, **661**, 1 (1963). [g] E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3253 (1958). [h] S. Brownstein, *Can. J. Chem.*, **38**, 1590 (1960).

Secondary Deuterium Kinetic Isotope Effects. Table IV shows the α and β secondary deuterium kinetic isotope effects for the chromyl chloride oxidation of **10** and **11**.

Table IV. Secondary Deuterium Kinetic Isotope Effects in Carbon Tetrachloride[a]

Substrate	$k_\psi \times 10^2$ sec^{-1}	k_2,[b] M^{-1} sec^{-1}	k_H/k_D
Styrene (**4**)[c]	10.38	24.01	
α-Deuteriostyrene (**10**)[d]	9.86	24.43	0.98
β,β-Dideuteriostyrene (**11**)[e]	11.1	27.18	0.88

[a] [CrO_2Cl_2] = 4.0×10^{-4} *M*, λ = 415 mμ, T = 0.0 ± 0.02°. [b] Second-order rate constant = k_ψ/[styrene]. [c] [**4**] = 4.34×10^{-3} *M*. [d] [**10**] = 4.03×10^{-3} *M*. [e] [**11**] = 4.08×10^{-3} *M*.

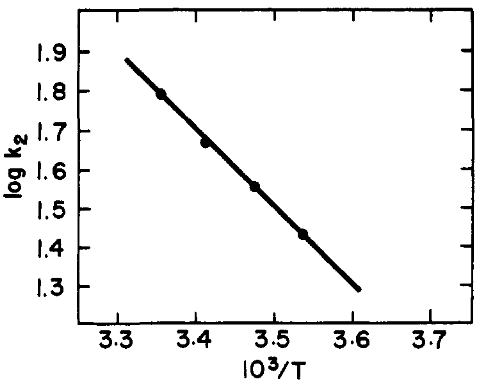


Figure 1. Plot of log k_2 *vs.* the reciprocal of temperature for the chromyl chloride oxidation of styrene.

Discussion

The rates of the chromyl chloride oxidation of 12 styrenes in carbon tetrachloride solution are shown in Table II. It is seen that electron-releasing groups accelerate the rate and that electron-attracting groups slow the rate ($\rho^+ = -1.99$).[1] The table also shows that α-methylstyrene (**14**) is oxidized at a rate comparable to *trans*-β-methylstyrene (**15**), seven times as fast as **4**, and four times as fast as *cis*-β-methylstyrene (**16**).[35] Resonance stabilization of a partial positive charge at the tertiary benzylic carbon atom probably explains the greater reactivity of **14** over **4**, and the faster rate of oxidation of **15** *vs.* **16** is probably explicable in terms of steric factors.

It must be noted that the relative reactivities of cis and trans isomers are not always a simple matter. For example, in contrast to the relative reactivity of **15** and **16**, *cis*- and *trans*-stilbene (**17** and **18**) show the reverse order of reactivity with chromyl chloride. The greater reactivity of **17** over **18** has also been observed in bromine addition,[35–38] and in peracetic acid oxidation.[39,40] In contrast, **18** reacts faster than **17** in chromic acid oxidation[41] and in cis 1,3-dipolar cycloadditions.[42] It must also be pointed out that neither **17** nor **18** gives the expected rearranged carbonyl products when oxidized with chromyl chloride under the previously reported experimental conditions.[8,43,44] However, using different reaction conditions, Nenitzescu and coworkers have successfully oxidized **17** and **18** to carbonyl compounds with chromyl chloride.[47]

Substitution of a phenyl group for a hydrogen atom on the benzylic carbon atom of **4** increases the rate of oxidation by a factor of approximately 13. This rate enhancement could arise from resonance stabilization

---

(35) The relative rate for the electrophilic addition of bromine, which presumably proceeds *via* a three-membered ring activated complex with considerable carbonium ion character, to **4**, **14**, **15** and **16** is 1:60.7:1.1:0.79.[36–38]

(36) J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1483 (1969).

(37) J. E. Dubois and A. Schwarcz, *Tetrahedron Lett.*, 2167 (1964).

(38) J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 2944 (1970).

(39) D. Swern, *J. Amer. Chem. Soc.*, **69**, 1692 (1947).

(40) J. Boeseken and J. S. P. Blumberger, *Recl. Trav. Chim. Pays-Bas*, **44**, 90 (1925).

(41) A. K. Awasthy and J. Rocek, *J. Amer. Chem. Soc.*, **91**, 991 (1969).

(42) Reference 14, p 19.

(43) Table I, footnote *v*.

(44) The lack of reactivity of **17** and **18** presumably is due to low solubility and polymerization.[4,45,46]

(45) Table I, footnote *c*.

(46) A. Ghenciulescu, I. Necsoiu, M. Rentea, and C. D. Nenitzescu, *Rev. Roum. Chim.*, **14**, 1543 (1969).

(47) Table V, footnotes *d* and *e*.

by the phenyl groups of a developing positive charge at the tertiary benzylic carbon atom. Rate retardation due to steric factors is observed when two and three phenyl groups are successively added to **4** (tri- and tetraphenylethane). 3-Phenylpropene is oxidized at a rate comparable to alkenes[1] since the benzene ring is insulated from the center of unsaturation by a methylene group.

Comparison (Table V) of the relative rates of the chromyl chloride oxidation of 1,1-diphenylethene (**19**) and **4** with cis 1,3-dipolar cycloaddition reactions further mitigates against **8** as the possible activated complex.[15] When the same relative rates and the respective ρ values (Table V) are compared with reactions which are postulated to proceed *via* three-membered ring activated complexes, it is seen that the activated complex for the chromyl chloride oxidation of styrenes has less carbonium ion character than bromine addition and more cationic charge than dibromocarbene addition and epoxidation.[47]

Table V. Relative Reactivities of Styrene and 1,1-Diphenylethene in Reactions Involving Cyclic Three-Membered and Five-Membered Ring-Activated Complexes

Reaction	Ring size of activated complex	k_{19}/k_4	Reaction constant (ρ^+)
Chromyl chloride oxidation[a]	3 or 5[a]	12.8	−1.99
Bromine addition[b]	3	25	−4.30
Dibromocarbene addition[c]	3	2.0	
Epoxidation[d,e]	3	4.3	−1.3[e]
Chromic acid oxidation[f]	3	2.2	
Cis 1,3-dipolar cycloaddition of diphenylnitrilimine[g]	5	0.07	
Cis 1,3-dipolar cycloaddition of benzonitrile oxide[h]	5	0.35	
Cis 1,3-dipolar cycloaddition of diazodiphenylmethane[i]	5	0.2	
Cis 1,3-dipolar cycloaddition of C-phenyl-*N*-methylnitrone[j]	5	0.08	+0.9

[a] This work. [b] References 36 and 37. [c] P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, **78**, 5430 (1956). [d] Reference 14, p 775; B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955). [e] Y. Ishii and Y. Inamoto, *Kogyo Kagaku Zasshi*, **63**, 765 (1960); *Chem. Abstr.*, **58**, 4393 (1963). [f] Reference 41. [g] Reference 42. [h] Reference 14, p 826. [i] R. Huisgen, H. Stangl, H. J. Strum, and H. Wagenhofer, *Angew. Chem.*, **73**, 70 (1961). [j] Reference 14, p 865.

The low enthalpies of activation (2–9 kcal/mol) and the large negative entropies of activation (−20 to −42 eu) (Table II) are consistent with a highly ordered activated complex. These values are comparable to those observed in epoxidations,[48] in 1,3-dipolar cycloadditions,[16,49] and in the cycloaddition of permanganate ion to unsaturated carboxylate anions.[18] Thus, it is seen that structures **5** and **6** are consistent with the observed relative reactivities and the thermodynamic data.

In an attempt to further differentiate among **5** and **6**, we examined the effect of solvents (CS_2, CCl_4, $CHCl_3$, CH_2Cl_2) on the rate of chromyl chloride oxidation of **4** (Table III). Since solvent polarity and solvating power are not always well specified by the individual physical characteristics of the solvent, the rates were also compared with several empirical parameters for estimating solvent polarity. The data in Table III clearly show that the rate of oxidation is faster in the more polar solvents chloroform and methylene chloride. This is also consistent with the formation of partially charged activated complex (**5** or **6**) from the two neutral molecules (**4**) and chromyl chloride.

A partial change in hybridization of the reactant carbons from sp^2 to sp^3 between the ground state and activated complex is predicted on theoretical grounds to give an inverse secondary deuterium kinetic isotope effect ($k_H/k_D < 1$).[48,50–58] Thus, one might expect an initial attack of chromyl chloride at the terminal carbon (β carbon) of **10** or **11** with concomitant development of a partial positive charge at the benzylic carbon atom (α carbon), would lead to a small or negligible secondary deuterium isotope effect for the oxidation of **10** and an inverse secondary deuterium kinetic isotope effect for the oxidation of **11**. A small secondary deuterium isotope effect for the oxidation of **10** is reasonable since the benzylic carbon atom retains a nominal sp^2 hybridization during an initial attack of chromyl chloride at the β carbon atom. This argument is consistent with the absence of secondary deuterium kinetic isotope effects in radical reactions at carbon–carbon double bonds.[59–62] Presumably in reactions of this type the carbon atom becoming the site of the new radical is still essentially sp^2 hybridized in the transition-state region.

The observed $k_H/k_{\alpha\text{-D}} = 0.98$ for **10** and the $k_H/k_{\beta\text{-D}} = 0.88$ for **11** are in complete accord with the above predictions. That is, in the rate-limiting step the oxygen atom of chromyl chloride attacks the β-carbon atom and the rehybridization progresses from sp^2 toward sp^3 as the new bond is being formed. At the same time the hybridization at the benzylic carbon atom is essentially sp^2 since it is going from an olefinic center to some carbonium ion like character. Consequently, it appears that the secondary deuterium kinetic isotope effects are consistent with the formulation of **5** or **6** as the activated complex for the formation of the 1:1 chromyl chloride–styrene adduct (**3**).

Although the oxidations of carbon–carbon double bonds by chromic acid, chromyl acetate, and chromyl chloride give different products due to the diverse reaction conditions, it is not unreasonable to consider the possibility of similar reaction pathways for the three oxidants. The cyclic epoxide-like three-membered ring activated complexes **20**, **21**, and **22** have been proposed for the chromic acid oxidation of alkenes in aqueous and in acetic acid solutions.[41,63] However, it

---

(48) W. F. Bayne, *Tetrahedron Lett.*, 2263 (1970).

(49) A. Battaglia and A. Dondoni, *Ric. Sci.*, **38**, 201 (1968).

(50) W. R. Dolbier, Jr., and S-H. Dai, *J. Amer. Chem. Soc.*, **90**, 5028 (1968).

(51) D. B. Denney and N. Tunkel, *Chem. Ind.* (*London*), 1383 (1959).

(52) J. F. Baldwin and J. A. Kapecki, *J. Amer. Chem. Soc.*, **91**, 3106 (1961); **92**, 4874 (1970).

(53) K. Humski, R. Malojsic, S. Bercic, and D. E. Sunko, *ibid.*, **92**, 6534 (1970).

(54) A. Streitweiser, Jr., R. H. Jageen, R. C. Fahey, and S. Suzuki, *ibid.*, **80**, 2326 (1958).

(55) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

(56) E. R. Thornton, *Ann. Rev. Phys. Chem.*, **17**, 349 (1966).

(57) E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963).

(58) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960.

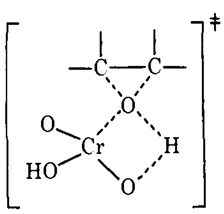
(59) W. A. Pryor, R. W. Henderson, R. A. Patsiga, and N. Carroll, *J. Amer. Chem. Soc.*, **88**, 1199 (1966).

(60) M. Feld, A. P. Stefani, and M. Swarc, *ibid.*, **84**, 4451 (1962).

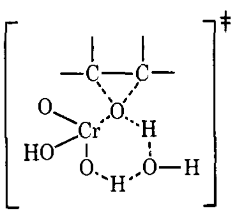
(61) M. Matsuoka and M. Swarc, *ibid.*, **83**, 1260 (1961).

(62) M. Takahaski and R. J. Cvetanovic, *Can. J. Chem.*, **40**, 1037 (1962).

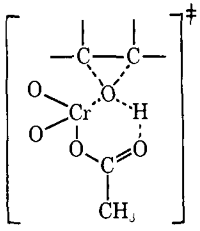
(63) Table I, footnotes *g*, *i*, and *w*.



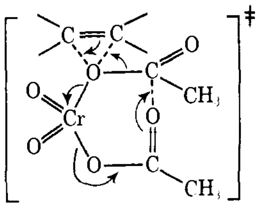
20



21



22



23

appears that a change in mechanism occurs in the chromic acid oxidation of styrenes.[41] An activated complex resembling **23** has been proposed for the chromyl acetate oxidation of alkenes and styrenes.[63,64] As stated above, **6** could also represent the activated complex in the rate-determining step for the chromyl chloride oxidation of alkenes and cycloalkenes. It is also of interest to note that epoxides have been isolated in the chromic acid oxidation of allylic alcohols,[65] cyclohexene,[66] and styrenes,[67] and in the chromyl acetate oxidation of alkenes and styrenes.[63,64] The carbonyl products obtained in the chromyl chloride oxidation could arise from isomerization of epoxide intermediates which could be formed from **5**, **6**, or **7**.

We conclude from the relative rates, the solvent effects, the thermodynamic data, the magnitude of the ρ^+ value, and the secondary deuterium kinetic isotope effects that the electrophilic addition of chromyl chloride to styrene probably involves an activated complex resembling **5** or **6** in the rate-determining step.

Acknowledgment. We express our thanks to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Fillmore Freeman also thanks California State College, Long Beach, for the award of a Special Leave for Faculty Research during this investigation.

(64) M. A. Davis and W. J. Hickinbottom, *J. Chem. Soc.*, 2205 (1958), and earlier papers in series.

(65) P. S. Kalsi, K. S. Kumar, and M. S. Wadia, *Chem. Ind.* (*London*), 71 (1971).

(66) J. Roček and J. C. Drozd, *J. Amer. Chem. Soc.*, **92**, 6668 (1970).

(67) Table I, footnotes *s* and *t*.

Titanocene as an Intermediate in Reactions Involving Molecular Hydrogen and Nitrogen

John E. Bercaw, Robert H. Marvich, Larry G. Bell, and Hans H. Brintzinger*

Contribution from the Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48104.

Received May 24, 1971

Abstract: The bis(cyclopentadienyl)titanium(II) species $[C_5(CH_3)_5]_2Ti$, $([C_5(CH_3)_5]_2Ti)_2$, and $[(C_5H_5)_2Ti]_2$ have been prepared and characterized. These species react reversibly with molecular hydrogen to form hydride complexes, with molecular nitrogen to yield intensely colored N_2 complexes, and irreversibly with carbon monoxide to form the respective dicarbonyl derivatives. Triphenylphosphine forms a complex of composition $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ with $[(C_5H_5)_2Ti]_2$. This phosphine complex reacts reversibly with H_2 to form a monomeric titanocene phosphine hydride, and irreversibly with N_2 and CO. $[(C_5H_5)_2Ti]_2$ rapidly exchanges cyclopentadienyl protons for deuterium in the presence of D_2. These unique reactions are utilized as a diagnostic to establish the occurrence of a transient titanocene species in other reaction systems in which the isolation of intermediates is not feasible. The participation of these Ti(II) sandwich compounds and their hydride derivatives in catalytic hydrogenation reactions and in the complexation and reduction of molecular nitrogen is discussed. The isolation and characterization of a titanocene ethyl complex, which is an intermediate in the Volpin–Shur nitrogen-reducing system, is reported, and evidence for the occurrence of $[(C_5H_5)_2Ti]_2$ in this system is described.

The unusual reactivity of reaction systems involving titanocene toward normally rather inert molecules such as H_2 and N_2 has recently been the subject of considerable interest. Reaction systems such as $TiCl_4$ with sodium cyclopentadienide,[1] $(C_5H_5)_2Ti(CO)_2$,[2] and $(C_5H_5)_2TiCl_2$ with various Grignard reagents[3] have been shown to catalytically hydrogenate alkenes and alkynes. The fixation and reduction of molecular nitrogen has been observed with mixtures of $(C_5H_5)_2TiCl_2$ and ethylmagnesium bromide and in other systems containing $(C_5H_5)_2Ti$ derivatives.[4–8] Highly reactive spe-

---

[1] M. E. Vol'pin, V. A. Dubovitskii, and O. V. Nogina, *Dokl. Akad. Nauk SSSR*, **151**, 1100 (1963).

[2] K. Sonogashira and N. Hagihara, *Bull. Chem. Soc. Jap.*, **39**, 1178 (1966).

[3] K. Shikata, K. Nishino, K. Azuma, and Y. Takegami, *Kogyo Kogaku Zasshi*, **68**, 358 (1965).

Brintzinger, et al. / Titanocene in H_2 and N_2 Reactions