One-Electron Reduction of Carbonium Ions. III. The Effect of Added Anions on the Rate of Reduction of the Tropylium Ion with Cr(II)[1]

Kunio Okamoto, Koichi Komatsu, Susumu Tsukada, and Osamu Murai
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606

(Received October 30, 1972)

The one-electron reduction of tropylium fluoroborate with Cr(II) was carried out in aqueous solution containing various anions (Cl^-, Br^-, SO_4^{2-}, HSO_4^-, BF_4^- and ClO_4^-) which were added as proton acids or as sodium salts, and the reaction rate at 25 °C was measured by the use of the flow method. It was found that Cl^-, Br^-, and SO_4^{2-} exhibit the characteristic rate-accelerating effect, whereas BF_4^- and ClO_4^- show a slight rate-retarding effect. From the extrapolation of the anion concentration to zero, it was indicated that this reaction can proceed even in the absence of added anions. From these findings, together with the results of chemical and spectrophotometrical analyses of the Cr(III) species, it was concluded that the reduction of the tropylium ion with Cr(II) proceeds through an electron-transfer step where the anion (Cl^-, Br^-, or SO_4^{2-}) or the water molecule acts as a weakly interacting electron-transfer bridge. This mechanism is essentially analogous to the "inner-sphere mechanism" known in the field of inorganic metal complex chemistry.

In the preceding paper,[2] we have reported on the reactivities of the cycloheptatrienyl and triphenylmethyl cations with a series of metallic powders and of the low-valent metallic ions, and demonstrated that the spectra of the reduction product yields may be regarded as a measure of the reducibility of the respective carbonium ions. As an extension of this work, a more quantitative investigation of the reducibility by the use of kinetic measurements seems of interest. Among the various reductants examined in the previous work, Cr(II) was found to be a satisfactory reagent, especially for kinetic measurements, since the one-electron reduction with Cr(II) proceeds quite readily without forming any by-product, as has already been reported in the case of some carbonium ions.[2,3] Prior to the kinetic study with respect to the reducibility of various stable carbonium ions, it seems necessary to clarify the mechanistic characteristics of this reaction by the use of a single representative carbonium ion, *e.g.*, the cycloheptatrienyl cation (the tropylium ion).

In the field of inorganic chemistry, the mechanisms for the reduction of several transition-metal complexes with Cr(II) are well established and are, in general, classified into "inner-sphere" and "outer-sphere" mechanisms depending upon whether or not an electron-transfer bridge between the reductant and the oxidant exists.[4]

On the other hand, for organic compounds, Cr(II) is known to be a potent and versatile reducing agent and has been used in the reduction of carbonium ions,[2,3] organic halides,[3c,5] olefins,[6] and carbonyl compounds.[6a] Among these reactions, the reduction of organic halides was interpreted as proceeding through reaction sequences analogous to the inner-sphere mechanism mentioned above, with the halide ion acting as an electron-transfer bridge between the organic moiety and Cr(II):[5a-d,g]

$$RX + Cr^{2+} \rightarrow [R\cdots X\cdots Cr]^{2+} \rightarrow R\cdot + CrX^{2+} \qquad (1)$$

It is currently accepted that the produced radical species is rapidly captured by the second chromous ion to furnish an organochromic complexes, which subsequently dimerizes with an unchanged halide or undergoes protonolysis to give a monomeric hydrocarbon.[3c,5c,e] There is also an exceptional case in which the first-formed radical abstracts the hydrogen atom before the formation of the organometallic complex.[5g]

In contrast to the reduction of organic halides, the chromous-ion reduction of carbonium ions usually gives rise to only dimers of the corresponding radicals,[2,3] but no kinetic investigation of this reaction has been reported. We chose the tropylium ion as a representative of stable carbonium ions and successfully measured the reduction rate with Cr(II) in an aqueous solution by the use of flow method; some findings of the effect of various added anions upon the reduction rate were obtained. The Cr(III) species produced under the various conditions were also analyzed chemically and spectrophotometrically. From the results obtained by these experiments, we wish to clarify the mechanism and scope of the reaction in this paper.

Results

Kinetic Measurements of the Reaction of the Tropylium Ion with Cr(II). As has already been reported,[2,3d] the tropylium ion reacts with Cr(II) quite rapidly

---

[1] Presented at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1969.

[2] Part II: K. Okamoto, K. Komatsu, and H. Shingu, This Bulletin, **42**, 3249 (1969).

[3] a) J. B. Conant and H. B. Cutter, *J. Amer. Chem. Soc.*, **48**, 1016 (1926), and the references cited therein; b) J. B. Conant and N. W. Bigelow, *ibid.*, **53**, 676 (1931); c) L. H. Slaugh and J. H. Raley, *Tetrahedron*, **20**, 1005 (1964); d) W. T. Bowie and M. Feldman, *J. Phys. Chem.*, **71**, 3696 (1967).

[4] a) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959); b) J. Halpern, *Quart. Rev.*, **15**, 207 (1961); c) F. Basolo and P. G. Pearson, "Mechanism of Inorganic Reactions," 2nd ed., John Wiley & Sons, New York, N. Y. (1967), Chap. 6.

[5] a) F. A. L. Anet and E. Le Blanc, *J. Amer. Chem. Soc.*, **79**, 2649 (1957); b) C. E. Castro, *ibid.*, **83**, 3262 (1961); c) C. E. Castro and W. C. Kray, *ibid.*, **85**, 2768 (1963); d) J. K. Kochi and D. D. Davis, *ibid.*, **86**, 5264 (1964), and the references cited therein; e) J. K. Kochi and D. Buchanan, *ibid.*, **87**, 853 (1965); f) R. P. A. Sneeden and H. P. Throndsen, *Chem. Commun.*, **1965**, 509; g) D. H. R. Barton, N. K. Basu, R. H. Hesse, F. S. Morehouse, and M. M. Pechert, *J. Amer. Chem. Soc.*, **88**, 3016 (1966), and the references cited therein.

[6] a) K. D. Kopple, *ibid.*, **84**, 1586 (1962); b) C. E. Castro, R. D. Stephens and S. Mojé, *ibid.*, **88**, 4964 (1966).

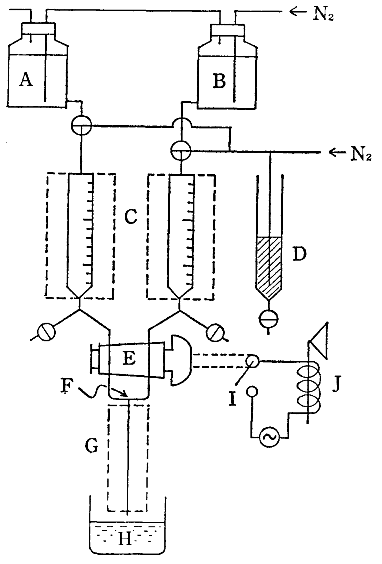

Fig. 1. A schematic diagram of "flow method" apparatus for the kinetic measurements.
A: the tropylium ion, B: Cr(II), C: water-jacketed burette, D: Hg, E: main stopcock, F: mixing chamber, G: water-jacketed reaction tube, H: "stop solution," I: knife switch connected to E, J: buzzer.

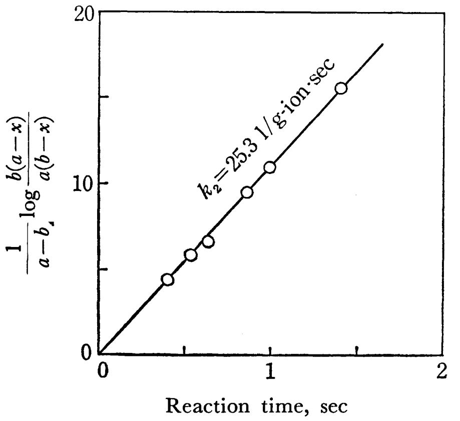

Fig. 2. The rate of the reaction of the tropylium ion with Cr(II) in 0.2 N HCl at 25 °C.
$[C_7H_7^+]_0 = 0.81 \times 10^{-2}$ g-ion/l
$[Cr(II)]_0 = 1.8 \times 10^{-2}$ g-ion/l

Table 1. The rate constants for the reaction of the tropylium ion with Cr(II) in aqueous acid solutions at 25°C

Solvent		Initial concentration		k_2
Acid,	N	$C_7H_7^+$ 10^{-2} g-ion/l	Cr(II) 10^{-2} g-ion/l	l/g-ion·sec
HCl	0.2	0.81	1.8	25.3
	1.7	0.71	1.6	63.2
	2.9	0.67	1.9	76.6
	2.9	1.8	3.0	74.1
	2.9	2.0	3.7	73.8
	4.4	0.65	1.0	83.0
HBr	0.2	0.85	1.6	24.6
	2.9	0.85	1.1	70.3
	2.9	0.68	1.7	68.0
H_2SO_4	0.05	0.99	3.2	24.9
	0.1	1.0	3.1	27.1
	0.6	1.2	2.1	22.6
	1.0	0.85	2.7	18.8
	1.8	0.81	2.9	14.3
HBF_4	0.2	2.0	4.0	8.6
	2.9	1.7	27	3.3
$HClO_4$	0.2	2.1	5.2	7.6
	1.2	2.4	5.4	4.3
	2.9	1.7	17	1.4

Table 2. The rate constants for the reaction of the tropylium ion with Cr(II) in the presence of anions added as sodium salts in aqueous acid solutions (0.2 N) at 25°C

Acid (0.2 N)	Added anion		Initial concentration		k_2
		g-ion/l	C_7H^+ 10^{-2} g-ion/l	Cr(II) 10^{-2} g-ion/l	l/g-ion·sec
HCl	Cl^-	0.0	0.81	1.8	25.3
		1.0	0.84	2.7	60.2
		2.5	0.56	1.4	84.0
		4.0	0.58	1.0	87.4
HBr	Br^-	0.0	0.85	1.6	24.6
		1.0	0.68	2.2	50.6
		1.8	0.93	1.7	65.1
		1.9	0.66	1.4	65.8
		3.4	0.57	1.3	65.8
		4.0	0.93	1.7	65.9
H_2SO_4	SO_4^{2-}	0.0	1.0	3.1	27.1
		0.3	0.92	1.9	45.5
		1.0	0.92	2.0	58.0
		1.6	0.82	2.1	64.4
H_2SO_4	HSO_4^-	0.3	0.90	1.9	33.8
		1.0	0.90	1.8	35.0
		2.0	0.93	1.8	32.9
		3.5	0.88	2.2	26.0
HBF_4	BF_4^-	0.0	2.0	4.0	8.6
		1.0	1.9	4.5	6.4
		2.5	2.2	4.4	3.5
		4.5	1.8	5.4	1.4
$HClO_4$	ClO_4^-	0.0	2.1	5.2	7.6
		2.8	2.5	3.5	2.1

and quantitatively to give the dimer, bitropyl. The kinetic measurement of this reaction was made at 25 °C by the use of the apparatus depicted in Fig. 1. The aqueous acid solutions of the tropylium ion and of Cr(II) were mixed in a T-shaped mixing chamber and then allowed to react while flowing down through a reaction tube. The reaction time was 0.2—1.5 sec, depending on the length of the tube. After the quenching of the reaction by the use of the instantaneous oxidation of the unchanged Cr(II) with an aqueous solution of $CuSO_4$,[7] bitropyl was extract-

---

[7] It was ascertained that Cu(II) has no interaction with unchanged tropylium ion under these conditions; see the Experimental section. The reactions of Cu(II) with the tropyl radical, such as the one reported by Kochi and Rust (J. K. Kochi and F. F. Rust, *J. Amer. Chem. Soc.* **83**, 2017 (1961)), seem to be negligible, if present at all, because the coupling reaction of the tropyl radical is supposed to be so fast ($k_2 \sim 2 \times 10^7$ M^{-1} sec^{-1} (22 °C); M. L. Morrell and G. Vincow, *J. Amer. Chem. Soc.*, **91**, 6389 (1969)) that, at this stage of the reaction, the steady-state concentration of the radical must be negligibly small compared with the concentration of the tropylium ion or bitropyl.

ed with *n*-hexane and determined by ultraviolet spectroscopy. The initial concentrations of both the reagents were set so that the concentration of Cr(II) would be 1.5 to 3.0 fold greater than that of the tropylium ion. The results for the various reaction times were treated according to the ordinary second-order rate equation (first-order for each reagent) to give a good straight line through the point of origin, as is shown in Fig. 2. The reaction conditions and the graphically-obtained values of the second-order rate constants are listed in Tables 1 and 2.

In a representative run, the unchanged tropylium ion was determined from the ultraviolet spectrum of the aqueous layer, and the material balance was found to be >97.5%. The product, bitropyl, was characterized on the basis of its infrared spectrum, the purity being ascertained by thin-layer chromatography.

The Effect of Added Anions on the Reduction Rate. In order to obtain information on the mechanism operating, especially at the electron-transfer step, the reaction of the tropylium ion with Cr(II) was carried out in aqueous acid solutions containing various anions (Cl^-, Br^-, SO_4^{2-}, HSO_4^-, BF_4^-, and ClO_4^-), which were added as proton acids or as sodium salts; the effects of the concentrations and of the nature of the anions upon the rate of the reaction were then examined. Among the results shown in Tables 1 and 2 and in Figs. 3 and 4, the following are noteworthy: (a) Cl^-, Br^-, and SO_4^{2-} have the characteristic effect of increasing the rate of the reaction; (b) this rate-increasing effect approaches its maximum as the concentration of the anion is increased; (c) on the contrary, BF_4^- and ClO_4^- show only a slight rate-retarding effect; (d) the extrapolation of the concentration of each anion leads to the same intercept where $k_2=9$ (l/g. ion.sec) at 25 °C; (e) H_2SO_4 and HSO_4^- seemingly exhibit a rate-accelerating effect at lower concentrations and a rate-retarding effect at higher concentrations. Among these findings, the observation (d) clearly indicates that the presence of halide ions is not essential for the reduction of the tropylium ion, as has been reported in the cases of the triphenylmethyl and diphenylmethyl cations.[3c)] This result is in sharp contrast to the observation made by Castro[6b)] that the 1,1-diphenylethyl cation can not be reduced by Cr(II) unless the chloride ion is added. The characteristic effect shown by H_2SO_4 and HSO_4^- as described in (e) seems to be attributable to the equilibrium composition[8)] of H_2SO_4, HSO_4^-, and SO_4^{2-} in an aqueous solution; at lower concentrations, the SO_4^{2-} ion, which is predominant as a result of the nearly complete dissociation of H_2SO_4 or HSO_4^-, exerts a rate-accelerating effect, whereas at higher concentrations, undissociated H_2SO_4 and HSO_4^- seem to retard the reaction.

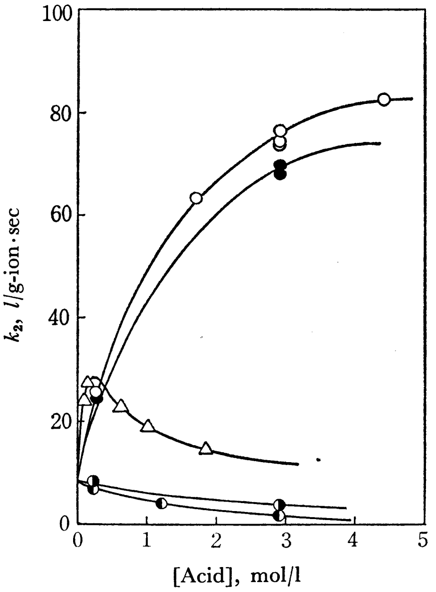

Fig. 3. The effect of anions added as proton acids on the reaction rate.
○: HCl, ●: HBr, △: H_2SO_4, ◑: HBF_4, ◐: $HClO_4$.

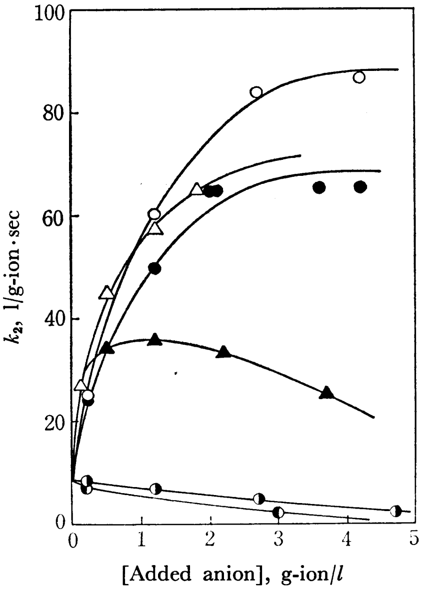

Fig. 4. The effect of anions added as sodium salts on the reaction rate.
○: Cl^-, ●: Br^-, △: SO_4^{2-}, ▲: HSO_4^-, ◑: BF_4^-, ◐: ClO_4^-.

The Analysis of Cr(III) Species. Although Cr(II) is labile to the substitution of its ligands, Cr(III) is known to be sluggish to ligand substitution.[9)] Thus, the analysis of the group attached to Cr(III), which is produced as a result of Cr(II) reduction, makes it possible to deduce the nature of the activated complexes. Taking advantage of these properties, Taube and his coworkers[10)] successfully demonstrated that one-electron transfer reactions from Cr(II) to several inorganic metallic complexes proceed through an activated complex in which a single anion or a molecule acts as an electron-transfer bridge. With the expectation of obtaining information on the function of the added chloride ion on the electron-transfer step, we conducted the reaction of Cr(II) with an excess of the tropylium ion in variable HCl concentrations at room

---

[8)] "Gmelins Handbuch der anorganischen Chemie," 8 Auflage, System Nr. 9, Schwefel, Teil B–2, Verlag Chemie, GmbH., Weinheim (1960), p. 737.

[9)] H. Taube and H. Myers, *J. Amer. Chem. Soc.*, **76**, 2103 (1954).

[10)] Ref. 9; H. Taube, *ibid.*, **77**, 4481 (1955).

temperature and analyzed the Cr(III) species chemically and by their visible spectra.

An excess of the tropylium ion was allowed to react with Cr(II) in 0.1 to 2.9 M aqueous HCl for 10 min (more than 100 half-lives) under nitrogen; after the subsequent extraction of the organic product, the visible spectrum of Cr(III) was taken. As is shown in Table 3 and Fig. 5, the absorption maximum of Cr(III) at longer wavelengths was found to make a bathochromic shift to 605 mμ, which corresponds to $CrCl(H_2O)_5^{2+}$,[11] with an increase in the concentration of HCl. This indicates that the Cr(III) species formed at lower HCl concentrations is a mixture of $Cr(H_2O)_6^{3+}$ (λ_{max} 575 mμ[11]) and $CrCl(H_2O)_5^{2+}$, but at higher HCl concentrations most of the Cr(III) exists as $CrCl(H_2O)_5^{2+}$. The results of the chemical analysis of the chloride ion attached to Cr(III) exhibit qualitatively the same tendency, as is shown in Table 4.

TABLE 3. THE EFFECT OF THE HCl CONCENTRATION ON THE VISIBLE SPECTRA OF Cr(III) FORMED BY THE REACTION OF THE TROPYLIUM ION WITH Cr(II)

Initial concentration			λ_{max} for Cr(III) mμ
[HCl] N	$[C_7H_7^+]$ g-ion/l	[Cr(II)] g-ion/l	
0.07	0.026	0.014	588
0.14	0.080	0.051	592
0.26	0.080	0.050	595
0.40	0.080	0.050	598
0.55	0.080	0.047	602
0.58	0.080	0.048	602
2.90	0.047	0.029	606

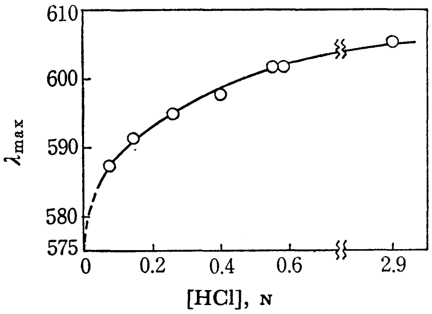

Fig. 5. The effect of HCl concentration on λ_{max} of Cr(III).

TABLE 4. THE EFFECT OF THE HCl CONCENTRATION ON THE AMOUNT OF THE CHLORIDE ION BOUND TO Cr(III)[a]

[HCl] N	Ratio of Cl bound to Cr(III) to total Cr(III)
0.072	0.47
0.110	0.51
0.139	0.53
0.175	0.59

a) [Cr(II)]: 0.014 g-ion/l, $[C_7H_7^+]$: 0.025 g-ion/l.

Discussion

One of the simplest mechanisms for the formation of bitropyl by the reduction of the tropylium ion with Cr(II) is the radical mechanism shown below:

$$C_7H_7^+ + Cr(II) \rightarrow C_7H_7\cdot + Cr(III) \qquad (2)$$

$$2C_7H_7\cdot \rightarrow (C_7H_7\text{-})_2 \qquad (3)$$

At present, it still remains open whether the radical produced is entirely free or is loosely affiliated with the metal ion (Step (4)); consequently, the possibilities for the reactions through $[C_7H_7\cdots Cr\cdots]^{2+}$, depicted in Steps (4) and (5) or in Steps (4) and (6), can not be rigorously eliminated:

$$C_7H_7\cdot + Cr(II) \rightarrow [C_7H_7\cdots Cr\cdots]^{2+} \qquad (4)$$

$$[C_7H_7\cdots Cr\cdots]^{2+} + C_7H_7\cdot \rightarrow (C_7H_7\text{-})_2 + Cr(II) \qquad (5)$$

$$[C_7H_7\cdots Cr\cdots]^{2+} + C_7H_7^+ \rightarrow (C_7H_7\text{-})_2 + Cr(III) \qquad (6)$$

Among these, however, Steps (2) and (3) seem most likely because, regardless of the acidity of the solvent, the reduction only gives the dimer, and no protonolysis product (tropilidene) which can be derived from $[C_7H_7\cdots Cr\cdots]^{2+}$ is ever formed. Furthermore, the marked effect of the added anions on the reaction rate indicates that, in any case, the rate-determining step is Step (2), at which an anion can substantially participate.

A representative example of such an anion-affected reaction may be seen in the reduction of $[Co(NH_3)_5X]^{2+}$ with Cr^{2+}. In this case the transition state in which the anion, X, acts as an electron-transfer bridge has been proposed:[10]

$$[Co(NH_3)_5X]^{2+} + Cr^{2+} + 5H^+ \rightarrow Co^{2+} + CrX^{2+} + 5NH_4^+ \qquad (7)$$

Also, in the present study, the fact that only such anions as Cl^-, Br^-, and SO_4^{2-}, which can coordinate with Cr(III), show the rate-accelerating effect would imply that these anions act as electron-transfer bridges between the tropylium ion and Cr(II). On the other hand, when the anion concentration is graphically extrapolated to zero, the rate constant still has the value of 9 (l/g.ion·sec), indicating that the electron transfer also takes place via the H_2O molecule as a bridge. Thus, in the reaction system, paths which proceed *via* an anion bridge and those which proceed *via* an H_2O bridge are both present; they give rise to $Cr(H_2O)_5X^{2+}$ and $Cr(H_2O)_6^{3+}$ respectively.

The effect of the added chloride ion on the reaction rate, however, is at most a factor of about 10 (see Fig. 4), much smaller than the factor of 10^6 found in the reaction (7) for the Cl bridging relative to the H_2O

---

[11] J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XI, Longmans, Green and Co., London (1954), p. 378.

bridging.[12] This may indicate that, although there is bridging by the chloride ion between $C_7H_7^+$ and Cr(II), it is much less effective than in the case of the reduction of $[Co(NH_3)_5X]^{2+}$, since even in the activated complex, the interaction between $C_7H_7^+$ and Cl^- is considered to be quite weak because of the complete delocalization of the positive charge in the tropylium ion.

When the reaction is conducted in the presence of HCl, the reacting species which gives rise to the chloride ion bridge is supposed to be $Cr(H_2O)_5Cl^+$[13] or the ion pair, $C_7H_7^+\cdots Cl^-$,[14] which is in equilibrium with $Cr(H_2O)_6^{2+}$ or with $C_7H_7^+$ respectively:

$$Cr(H_2O)_6^{2+} + Cl^- \rightleftarrows Cr(H_2O)_5Cl^+ + H_2O \qquad (8)$$

$$C_7H_7^+ + Cl^- \rightleftarrows C_7H_7^+\cdots Cl^- \qquad (9)$$

Therefore, it may be supposed that, among these species, the following reaction paths (Steps (10)—(12)) are competing with each other:

$$C_7H_7^+ + Cr(H_2O)_6^{2+} \rightarrow [C_7H_7\cdots \overset{H}{\underset{H}{O}}Cr(H_2O)_5]^{3+}$$

$$\rightarrow C_7H_7\cdot + Cr(H_2O)_6^{3+} \qquad (10)$$

$$\begin{tikzcd} C_7H_7^+\cdots Cl^- + Cr(H_2O)_6^{2+} \arrow[dr, "-H_2O"] & \\ & {[C_7H_7\cdots ClCr(H_2O)_5]^{2+}} \\ C_7H_7^+ + CrCl(H_2O)_5^+ \arrow[ur] & \end{tikzcd}$$

$$\rightarrow C_7H_7\cdot + CrCl(H_2O)_5^{2+} \qquad (11)$$

$$\begin{tikzcd} & {[C_7H_7\cdots ClCr(H_2O)_5]^{2+}} \\ & \rightarrow C_7H_7\cdot + CrCl(H_2O)_5^{2+} \quad (12a) \\ C_7H_7^+\cdots Cl^- + CrCl(H_2O)_5^+ \arrow[uur, "-Cl^-"] \arrow[dr, "-H_2O"'] & \\ & {[C_7H_7\cdots ClCrCl(H_2O)_4^+} \\ & \rightarrow C_7H_7\cdot + CrCl_2(H_2O)_4^+ \quad (12b) \end{tikzcd}$$

Path (10) proceeds by means of bridging with H_2O, while Paths (11) and (12) make use of the chloride bridge. As for Path (12), it can not be determined from the analysis of Cr(III) which course, (12a) or (12b), is pertinent, since $CrCl_2(H_2O)_4^+$ is known to react readily ($k_2 \approx 10^2$ l/g.ion·sec at 2 °C[9]) with Cr^{2+} to give $CrCl(H_2O)_5^{2+}$, as is shown below:

$$CrCl_2(H_2O)_4^+ + Cr^{2+} \rightarrow$$
$$CrCl(H_2O)_5^+ + CrCl(H_2O)_5^{2+} \qquad (13)$$

The tendency of the rate-increasing effect of anions to approach its maximum with an increase in the anion concentration (shown in Figs. 3 and 4) can be ascribed to the shift of the equilibria (8) and (9) to the right, with the result that the reaction proceeds completely *via* the bridging with the chloride ion so that no more rate acceleration becomes observable. This is also consistent with the result, obtained from the chemical analysis, that the amount of the chloride ion attached to Cr(III) increases with an increase in the HCl concentration.

From these results, it is concluded that the one-electron reduction of the tropylium ion with Cr(II) in the aqueous acid of the appropriate concentration does not occur directly between the two reagents, but proceeds by means of the electron-transfer bridge mechanism. Therefore, it may be expected that, so long as the acid solution is used in a concentration sufficient for the bridging, the reactivity of the various stable carbonium ions in this reaction will mainly reflect the inherent electron affinity of the respective carbonium ions, and that the effect of the steric factor will be minimized. The investigation on the correlation of such a reactivity with the electron affinity of the various stable carbonium ions is now in progress and will be reported in the following paper.

Experimental[15]

Materials. Tropylium fluoroborate was prepared from tropilidene according to the method of Conrow.[16] The aqueous solutions of the chromous ion were prepared by the dissolution of chromium metal (99.99%, Nakarai Co., Ltd.) in 2.9 M respective acid solutions under nitrogen after activation in 2.9 M HCl and rinsing with distilled water. The transfer and dilution of the original chromous solution were done by the use of a hypodermic syringe; distilled water or acid solutions of appropriate concentrations had previously been deoxygenated with nitrogen. The aqueous solutions of hydrochloric, hydrobromic, sulfuric, perchloric, and fluoroboric acids, the sodium salts of the respective anions, and the sodium bisulfate were of a reagent grade and were used without further purification.

Kinetic Measurements for the Reaction of the Tropylium Ion with Cr(II). The reaction was carried out under a nitrogen atmosphere in the flow system shown in Fig. 1. Burettes and a reaction tube were covered with jackets circulated with water thermostated at 25.0±0.2 °C. The aqueous acid solutions of the tropylium ion and of the chromous ion, the concentrations of which had been determined by ultraviolet spectroscopy and by iodometry, respectively, were charged into each burette from the reservoirs and let stand for at least 10 min for temperature equilibration. The nitrogen pressure in the whole system was raised to 200 mmHg above atmospheric pressure, and then the main stopcock was opened for about 4 sec so that 20 ml each of the reagent solutions ran into a glass reaction tube 3.6 mm in inner diameter, through a mixing chamber made of T-shaped glass tube 1.0 mm in inner diameter. The reagents were allowed to react for 0.3—1.5 sec while flowing through reaction tubes of various lengths; then they flowed out into 20 ml of a magnetically-stirred "stop solution" containing 0.5 M $CuSO_4$. The operation of the main stopcock was synchronized with a buzzer switch; while the stopcock was opened the buzzer sound was recorded on a tape recorder, and from the distance of the recording tape between the starting and ending points of the buzzer sound the flowing time of the reagents was

---

[12] J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Amer. Chem. Soc.*, **86**, 1019 (1964).

[13] H. L. Schlafer and H. Skoludek, *Z. Phys. Chem.* (Frankfurt am Main), **11**, 277 (1957).

[14] The formation of such an ion pair can be well supposed from the observation that the charge-transfer complexes are formed between the tropylium ion and halide ions (K. M. Harmon, F. E. Cummings, D. A. Davis, and D. J. Diestler, *J. Amer. Chem. Soc.*, **84**, 120, 3349 (1962); E. M. Kosower, *J. Org. Chem.*, **29**, 956 (1964)).

[15] The infrared and ultraviolet spectra were obtained on Shimadzu models IR-27 and UV-50M spectrometers respectively. The Kohlrausch bridge used for the conductometry was a Shimadzu apparatus, model BF-62.

[16] K. Conrow, "Organic Syntheses," Vol. 43, p. 101 (1963).

determined. The time-distance calibration was made by the use of the standard time service of the Nippon Telegram and Telephone Corporation. Thus, when the time required for a total flow of 40 ml was determined to be 4.00 sec, for example, the reaction times were calculated to be 0.26, 0.36, 0.46, 0.60, 0.72, and 1.04 sec with reaction tubes of the length of 25.1, 35.1, 45.0, 58.8, 70.2, and 102.5 cm respectively. The reaction solution was extracted three times with 50-ml portions of *n*-hexane, washed with three 100-ml portions of 10% aqueous sodium chloride, and dried over magnesium sulfate. The solvent was evaporated under reduced pressure to give white crystals which were identified as bitropyl from the superimposability of the infrared spectrum with the spectrum of an authentic sample. The amount of the product was determined by ultraviolet spectroscopy in ethanol, using 255 mμ (ε=7080) as a characteristic band for bitropyl.[17] The rate constants were determined graphically from the ordinary second-order rate equation. The efficiency of mixing in the mixing chamber was examined by the method described by Roughton,[18] *i.e.*, the measurement of the heat of neutralization, which was evolved when equivalent aqueous solutions of HCl and NaOH were mixed together under the same conditions as in the chromous-ion reduction. It was confirmed that 100% mixing was attained within 0.02 sec after mixing.

Test for the Efficiency of the Quenching of Cr(II) with Cu(II). To 20 ml of a 2.9 M HCl solution of the tropylium ion (0.02 g.ion/l) and $CuSO_4$ (0.5 mol/l), was added 10 ml of a 2.9 M HCl solution of Cr(II) (0.04 g.ion/l) under an atmosphere of nitrogen at room temperature. After 10 min, the ultraviolet spectrum of an aliquot showed that the amount of the tropylium ion had not been affected.

The Analysis of Cr(III) Complex in Solution. By the use of an apparatus employed in the kinetic measurements, 40-ml portions each of a solution of the tropylium ion and of Cr(II) in aqueous hydrochloric acid of various concentrations were mixed and allowed to react for 10 min at room temperature under nitrogen in a Erlenmeyer flask, set under the mixing chamber. The initial concentrations of both reagents were set as is shown in Tables 3 and 4, so that the amount of the tropylium ion was a 1.5—1.8 fold excess. After the extraction of the organic product with three 60-ml portions of *n*-hexane, the aqueous layer was subjected to the measurement of its visible spectrum or to the chemical analysis of the chloride ion bound to Cr(III) as follows: the free chloride ions in the solution were first determined by conductometric titration with 0.1 M $AgNO_3$. The solution was then heated at 100 °C for 30 min and titrated again with 0.1 M $AgNO_3$. The differences in titers before and after the heating of the solution was regarded as corresponding to the amount of chloride ions bound to Cr(III).[9]

---

[17] W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **79**, 352 (1957).

[18] F. J. W. Roughton, "Technique of Organic Chemistry," Vol. 8, ed. by A. Weissberger, John Wiley & Sons, New York, N. Y. (1963), p. 711.