

which is greater than the yield of $c\text{-C}_6\text{H}_{12}^+$ ions due to the additional $n\text{-C}_4\text{H}_{10}$ generated *via* process 33. However, in static systems at higher total pressures the ion-pair yield for $n\text{-C}_4\text{H}_{10}$ is 1.00,¹⁹ indicating that the $[\text{C}_6\text{H}_{10}\text{-C}_4\text{H}_8]^+$ complex, which dissociates into C_6H_8^+ and C_4H_{10} under our conditions, is quantitatively stabilized at much higher collision frequencies.

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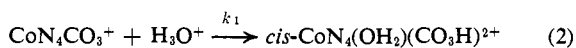
The Kinetics and Mechanism of Aquation of Carbonato Complexes of Cobalt(III). III. The Acid-Catalyzed Aquation of Some Carbonatobis(diamine)cobalt(III) Complexes

V. S. Sastri¹ and G. M. Harris

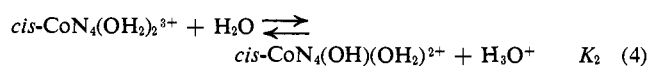
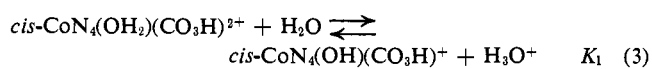
Contribution from the State University of New York at Buffalo, Buffalo, New York 14214. Received September 2, 1969

Abstract: This study has comprised examination of the aquation of the complex ions $\text{CoN}_4\text{CO}_3^+$, where $\text{N}_4 \equiv (\text{en})_2$, $(\text{pn})_2$, or $(\text{tn})_2$ ($\text{en} \equiv$ ethylenediamine, $\text{pn} \equiv$ propylenediamine, and $\text{tn} \equiv$ trimethylenediamine). The kinetics and mechanism appear to be identical over the range $1 < \text{pH} < 5$ with those of the tetraammine analog ($\text{N}_4 \equiv (\text{NH}_3)_4$), for which the experimental rate constant is given by $k = k_0 + k_1[\text{H}^+]$, as previously reported. The values of the rate parameters for the water-catalyzed part of the process are the same within the inescapably large experimental error for all four complexes, with $k_0 \cong 1 \times 10^{-4} \text{ sec}^{-1}$, $\Delta H_0^\ddagger \cong 16 \text{ kcal/mol}$, and $\Delta S_0^\ddagger \cong -20 \text{ eu}$. The acid-catalyzed reactions show some small but significant differences such that k_1 is a little smaller at 25° for the $(\text{en})_2$ and $(\text{pn})_2$ species ($0.5 \text{ M}^{-1} \text{ sec}^{-1}$) than for $(\text{tn})_2$ ($0.8 \text{ M}^{-1} \text{ sec}^{-1}$), and only about one-third as large as for the tetraammine ($1.5 \text{ M}^{-1} \text{ sec}^{-1}$), though the other rate parameters are not far apart. Deuterium solvent isotope effect studies confirm the earlier conclusion that these aquations involve a rate-determining proton transfer rather than a proton-preequilibrium mechanism.

Our most recent paper in this series² reported a study of the acid-catalyzed aquation of carbonato-tetraamminecobalt(III) ion over the acidity range $1 < \text{pH} < 5$. A combination of spectrophotometric and acidometric rate studies substantiated a stepwise concept for the reaction, with the rate-determining processes being ring opening of the chelated carbonato ligand by the parallel reactions ($\text{N}_4 = (\text{NH}_3)_4$)



The other reactions involved, all much more rapid than (1) and (2), consist of two acid-base equilibria and the decarboxylation of the product of reaction 2, *viz.*



(1) Work done by V. S. Sastri as part of the Ph.D. requirement of the State University of New York at Buffalo, June 1966. Complete dissertation available from University Microfilms, Ann Arbor, Mich.

(2) Part II: T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, **91**, 3207 (1969).



The rate law based on this mechanism takes the form

$$k_{\text{obsd}} = k_0 + k_1[\text{H}^+] \quad (6)$$

and was shown in the previous study² to interpret the data very well.

In a preliminary report,³ we briefly discussed similar data obtained for the analogous species in which $\text{N}_4 \equiv (\text{en})_2$ ($\text{en} \equiv \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), utilizing a slightly more complex reaction scheme. We have now reexamined these data in the light of our extensive experiments with the tetraammine complex, and find the mechanism of reactions 1-5 above to be entirely satisfactory for the $(\text{en})_2$ case. Furthermore, results obtained with the closely related complexes in which $\text{N}_4 \equiv (\text{pn})_2$ or $(\text{tn})_2$ ($\text{pn} \equiv \text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_2$; $\text{tn} \equiv \text{NH}_2(\text{CH}_2)_3\text{NH}_2$) also fit well into the proposed general scheme. An added significant feature of this work is a deuterium solvent isotope effect study, which provides additional confirmation of the mechanistic interpretation presented.

(3) G. M. Harris and V. S. Sastri, *Inorg. Chem.*, **4**, 263 (1965).

Experimental Section

Carbonatobis(ethylenediamine)cobaltic chloride was prepared according to standard technique⁴ and purified by repeated recrystallization from aqueous solution. The propylenediamine analog was prepared in a similar manner⁵ except that purification had to be accomplished by repeated precipitation of the complex from aqueous solution by addition of an excess of 3:1 alcohol/ether mixture.⁶ The preparation of the (tn)₂ complex was done as previously described⁷ and purified by repeated crystallization from water. Analyses for cobalt were carried out by either the CoSO₄ or Co₃O₄ method, carbonate by the Fresenius technique, and chloride by weighing as AgCl.

Table I. Spectral Data for Complexes

Complex	Co(en) ₂ CO ₃ ⁺		Co(pn) ₂ CO ₃ ⁺		Co(tn) ₂ CO ₃ ⁺	
Wavelength, mμ	360	512	357	515	360	520
ε _{obsd}	121	133	135	144	127	108
ε _{lit.} (ref 5)	120	127	122	133	128	109

Table II. Derived Rate Parameter Values at 25°

	(NH ₃) ₄	(en) ₂	(pn) ₂	(tn) ₂
10 ⁴ k ₀ , sec ⁻¹	1.3 ± 0.2	1.2 ± 0.2	1.0 ± 0.2	0.8 ± 0.2
k ₁ , M ⁻¹ sec ⁻¹	1.5 ± 0.1	0.6 ± 0.05	0.5 ± 0.05	0.8 ± 0.05
ΔH ₀ [‡] , kcal/mol	12 ± 5	18 ± 3	18 ± 3	16 ± 3
ΔS ₀ [‡] , eu	-37 ± 19	-15 ± 9	-15 ± 9	-21 ± 9
ΔH ₁ [‡] , kcal/mol	15 ± 1	14 ± 3	14 ± 3	12 ± 3
ΔS ₁ [‡] , eu	-6 ± 4	-13 ± 9	-13 ± 9	-19 ± 9

Anal. Calcd for Co(en)₂CO₃Cl: Co, 21.48; CO₃, 21.80; Cl, 12.90. Found: Co, 21.8; CO₃, 21.7; Cl, 12.7. Calcd for Co(pn)₂CO₃·Cl·2H₂O: Co, 17.40; CO₃, 17.70; Cl, 10.46; H₂O, 10.64. Found: Co, 17.5; CO₃, 17.5; Cl, 10.4; H₂O, 10.7. Calcd for Co(tn)₂CO₃·Cl·H₂O: Co, 18.39; CO₃, 18.7; Cl, 11.07; H₂O, 5.62. Found: Co, 18.2; CO₃, 18.6; Cl, 11.0; H₂O, 5.4.

An additional purity check was provided by the visible absorption spectra, as determined both by Beckmann DU and Cary 14 or 15 spectrophotometers. The data for peak absorbances are given in Table I. All chemicals used were of reagent grade and the distilled water was purified by passage through a mixed-bed ion-exchange column.

The reactions were followed using Beckmann DU and Cary 15 spectrophotometers. Temperature was controlled to ±0.1° in the jacketed spectrophotometer cell as confirmed by thermocouple measurements. That the overall reaction consists of conversion to the complexes represented in reaction 4 was confirmed by comparing the final spectra at various pH's with those of *bona fide* samples of the *cis*-diaquo complexes prepared by Werner's method.⁸ Since the value⁹ of pK₂ is about 6, only a small proportion of the hydroxo-aquo species should appear below pH 5. This was confirmed by the relatively small changes in the absorbances of the diaquo complexes over the range 1 < pH < 5 at the wavelengths of the peaks of the corresponding carbonato complex near 500 mμ.¹⁰

Kinetic runs were commenced by quickly dissolving weighed portions of the CoN₄CO₃⁺ compound in a thermostated solution of the desired acidity. Up to pH 2, the acidity was established by HClO₄, but above that value buffering was provided by use of the appropriate volumes of 0.1 M citric acid and 0.2 M disodium hydrogen phosphate. Changes in optical density with time were plotted in the conventional first-order fashion.¹¹ Good straight

lines were obtained over about two half-times of reaction, and pseudo-first-order observed rate constants, *k*, were derived from their slopes. pH measurements of the reactant solutions were made with a Beckmann Model 76 expanded-scale pH meter. The ionic strength of the solutions was not adjusted other than by the addition of reagents. However, separate experiments showed that the rate constant is rather insensitive to ionic strength changes in the range 0.1 < *I* < 0.3 M, as was also found in the tetrammine study,² so such effects were ignored in this work.

The heavy water experiments were carried out in the standard fashion, except that 99.5% D₂O was used as solvent. The quantity of light water introduced by the addition of the reagents was less than 1%, so the medium was considered to be essentially pure heavy water.

Results and Discussion

Preliminary studies were made of the rate of aquation at 25° of each of the three complexes at a buffered pH close to 3, with the complex ion concentration varied between the limits 3 × 10⁻³ and 2 × 10⁻² M. The

values of *k* were identical within ±5%, confirming the expectation that the reaction is first order in complex ion concentration. In all subsequent runs, this concentration was set at the convenient value of 5 × 10⁻³ M. The variation of *k* with pH was then studied at 25° for each of the three complexes. The data for the (en)₂ species have already been given.³ Those for the (pn)₂ and (tn)₂ analogs are presented in Figure 1, where each plotted point represents a mean value of as many as five runs at a given pH.¹² A weighted least-squares analysis of the data¹³ on the basis of eq 6 leads to the rate constant figures given in Table II, where comparative data for the tetraammine complex² are also presented.

A temperature dependence study was made by measuring *k* at four temperatures and several different pH values for each of the three diamine complexes. Plots of log *k* vs. 1/*T* were then prepared at each pH value, and the derived *E*_a values were plotted as a function of pH. The apparent limiting values of *E*_a at high and low pH were then utilized to derive estimates of ΔH₀[‡], ΔS₀[‡], ΔH₁[‡], and ΔS₁[‡], respectively, as given in Table II. The solvent isotope effect experiments were performed at 25° at four different acidities for each of the three complex ion types under consideration. The data are as given in Table III.

(11) That is, by plots of log (D₀ - D_∞)/(D_t - D_∞) vs. time, where the D's are the observed optical densities at zero time, time *t*, and "infinite" time, respectively. The correct D_∞ values at each pH, as determined in the separate experiments (ref 10), were used.

(12) The total number of runs was about 50 for each complex. In the earlier reports,³ data at pH > 4.7 were recorded but are excluded in the present analysis, since our later studies show that complications in the reaction are involved in the high pH range due to reversibility of the decarboxylation process.

(13) Weighted according to the number of runs at each pH. The deviations were expressed in percentage form for the purposes of this analysis, since the errors in the measurements are more or less proportional to the magnitudes of the observed *k*'s.

(4) J. S. Holden and G. M. Harris, *J. Amer. Chem. Soc.*, **77**, 1934 (1955).

(5) G. Lapidus and G. M. Harris, *ibid.*, **85**, 1223 (1963).

(6) Owing to the high solubility of this complex in water, only a syrupy residue is obtained on attempts to recrystallize from aqueous solution.

(7) J. E. Boyle and G. M. Harris, *ibid.*, **80**, 782 (1958).

(8) A. Werner, *Chem. Ber.*, **40**, 2119 (1907).

(9) J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952). (Note that the *cis* form of the species greatly predominates, since the *cis/trans* ratio is about 58 for the diaquo complex).

(10) The observed absorbances change from 77 to 71 in this pH range for the (en)₂ complex at 512 mμ, from 75 to 74 for the (pn)₂ complex at 515 mμ, and from 53 to 62 for the (tn)₂ complex at 520 mμ.

Table III. Solvent Isotope Effect on the Rate Constants of Aquation of Carbonato Cobaltic Complex Ions

pH	Co(en) ₂ CO ₃ ⁺		Co(pn) ₂ CO ₃ ⁺		Co(tn) ₂ CO ₃ ⁺	
	k ^H /k ^D (obsd)	k ^H /k ^D (calcd)	k ^H /k ^D (obsd)	k ^H /k ^D (calcd)	k ^H /k ^D (obsd)	k ^H /k ^D (calcd)
1.69	3.3	3.2	3.2	3.2	3.2	3.2
2.76	2.0	2.3	1.9	2.5	2.2	2.5
3.63	1.9	1.5	1.8	1.6	2.0	1.6
4.63	1.3	1.3	1.2	1.3	1.3	1.3

It is seen from Table II that the values of k_0 for each of the four complex ions of the type $\text{CoN}_4\text{CO}_3^+$ are essentially identical within the unavoidably large experimental errors of the measurement. The rounded average value is $k_0 = 1 \times 10^{-4} \text{ sec}^{-1}$, and the ΔH_0^\ddagger and ΔS_0^\ddagger values are also experimentally indistinguishable, with rounded values of 16 kcal/mol and -20 eu , respectively. Oxygen-18 exchange experiments by McKenzie, O'Connor, and Odell¹⁴ in aqueous solutions of $\text{Co}(\text{NH}_3)_4\text{CO}_3\text{Cl}$ at 25° , pH 9, and $I = 0.1 \text{ M}$, are interpreted in terms of "reversible dissociation of carbonate, one end at a time, which is fast enough to make the three oxygen atoms kinetically equivalent with respect to exchange of oxygen atoms." They report a rate constant of $1.7 \times 10^{-5} \text{ sec}^{-1}$ for the rate-determining process, but do not specify its nature, though it is inferred to be ring opening. Actually, their rate constant, which is only one-sixth as great as our k_0 , is not far distant from the rate constant for pseudo-first-order carbonate exchange by aquation, as explained elsewhere.¹⁵ This near-equivalence of oxygen-18 and carbon-14 exchange rates suggests that McKenzie, *et al.*,¹⁴ could have really been measuring the rate of aquation of the complex ion, a rather incomplete reversible process at high pH.¹⁶ This is possible since "free" carbonate exchanges its oxygen atoms with solvent water much more rapidly than in the ligand form, as they themselves demonstrated. Alternatively, there could be oxygen exchange with the unopened chelated carbonate itself through reversible formation of an "ortho" acid by water addition, as suggested for the exchange of "outer oxygens" in chelate oxalate in the complex ion¹⁷ $\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}$. In the case of the carbonato complex, complete "jumbling" of the three oxygens is ensured by the rapidity with which reaction 1 above (and its reverse¹⁸) occurs.

It is of interest to note that the rate of water-catalyzed ring opening of the carbonato complex, while almost identical with that of the analogous chelated sulfato complex, is appreciably more rapid than that of the phosphato species, though still within an order of magnitude. Ring opening of $\text{Co}(\text{en})_2\text{SO}_4^+$ to give $\text{Co}(\text{en})_2\text{SO}_4 \cdot \text{OH}_2^+$ has a rate constant¹⁸ at 25° of $8 \times 10^{-5} \text{ sec}^{-1}$, while the corresponding rate constant¹⁹ for $\text{Co}(\text{en})_2\text{PO}_4^+$ is $2.5 \times 10^{-5} \text{ sec}^{-1}$ at 22.5° . Clearly

(14) D. McKenzie, C. O'Connor, and A. L. Odell, *J. Chem. Soc., A*, 184 (1966).

(15) K. V. Krishnamurty, G. M. Harris, and V. S. Sastri, *Chem. Rev.*, 70, 171 (1970).

(16) A value of about 10^{-3} has been given for the equilibrium constant of reaction 1 at 20° , pH 8.7, and $I = 0.1 \text{ M}$ for $\text{N} \equiv \text{en}$: H. A. Scheidegger and G. Schwarzenbach, *Chimia*, 19, 166 (1965).

(17) L. Damrauer, and R. M. Milburn, *J. Amer. Chem. Soc.*, 90, 3884 (1968).

(18) C. G. Barraclough and R. S. Murray, *J. Chem. Soc.*, 7047 (1965).

(19) S. F. Lincoln and D. R. Stranks, *Aust. J. Chem.*, 21, 57 (1968).

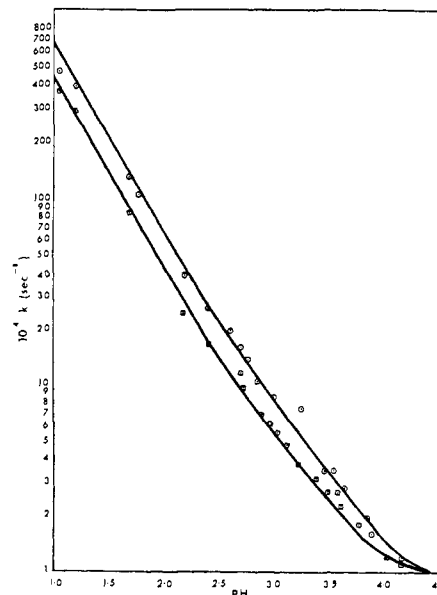
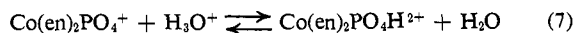


Figure 1. Variation of rate constant of aquation of $\text{Co}(\text{pn})_2\text{CO}_3^+$ and $\text{Co}(\text{tn})_2\text{CO}_3^+$ with pH at 25° : \square , $(\text{pn})_2$ complex; \circ , $(\text{tn})_2$ complex.

there are no substantial contrasts in the mechanisms of these processes.

The k_1 values for the various N_4 carbonato species show some small but significant differences. While the values for the $(\text{en})_2$ and $(\text{pn})_2$ species are experimentally indistinguishable at $0.55 \text{ M}^{-1} \text{ sec}^{-1}$ at 25° , the $(\text{tn})_2$ and $(\text{NH}_3)_4$ analogs show significantly greater rates, with $k_1 = 0.8$ and $1.5 \text{ M}^{-1} \text{ sec}^{-1}$, respectively. It is difficult to account for these variations by other than a qualitative stereochemical argument. Molecular models show that the amine protons may be appreciably closer to the coordinated oxygens of the carbonato group in the $(\text{tn})_2$ and $(\text{NH}_3)_4$ complexes as compared to the other two (which are identical in this respect). Perhaps this kind of "built-in" propensity for N-H...O hydrogen bridging promotes acid catalysis of carbonate ring opening in the acidic medium. However, it is noteworthy that the rate of carbonate exchange in basic medium^{5,7} is very much slower for the $(\text{tn})_2$ complex than for any of the other three. Here, the internal hydrogen bonding of the $(\text{tn})_2$ species must serve as a hindrance rather than a help to carbonate replacement, as suggested before.⁷ Certainly, it is clear from the present data that there can be very little relationship between the rate-determining process in acid-catalyzed aquation of $\text{CoN}_4\text{CO}_3^+$ complexes and that in the reversible carbonate release and return in basic solution. Also, there are considerable differences between the behavior of the carbonato complexes and the sulfato or phosphato analogs in acidic medium. Thus, ring opening of the complex ion $\text{Co}(\text{en})_2\text{SO}_4^+$ is completely insensitive to acid concentration¹⁸ over the range $1.3 < \text{pH} < 6$. However, $\text{Co}(\text{en})_2\text{PO}_4^+$ does exhibit an acid-catalyzed ring-opening process, which apparently results¹⁹ from a proton preequilibration according to



The pK of the protonated form is about 4 and the rate constant for its ring opening is about $6 \times 10^{-3} \text{ sec}^{-1}$ at 25° , nearly two orders of magnitude smaller than the corresponding value for $\text{Co}(\text{en})_2\text{CO}_3^+$.

The solvent isotope effect data presented in Table III are completely in keeping with expectation for hydrolysis reactions involving proton transfer in the rate-determining step. The total isotope effect on the observed rate constant is a combination of two effects, and can be expressed on the basis of eq 6 as follows.

$$k^H/k^D = (k_0^H + k_1^H[H^+]) / (k_0^D + k_1^D[D^+]) \quad (8)$$

At very low acid concentration, (8) reduces to the expression $k^H/k^D = k_0^H/k_0^D$. This ratio is seen to have a value of about 1.3 (Table III, data at pH 4.63), exactly of the order of magnitude to be expected for water-catalyzed hydrolyses.²⁰ In the more strongly acidic solutions, a contribution is made to the total isotope effect by the relative values of k_1^H and k_1^D . For a direct proton transfer mechanism, the ratio k_1^H/k_1^D can in theory be as high as 7, though smaller values are often observed.²¹ We assign a value $k_1^H/k_1^D = 3.3$

(20) E. R. Thornton, "Solvolysis Mechanisms," The Ronald Press Co., New York, N. Y., 1964, p 213.

(21) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapter XI.

and, using eq 8 and the requisite experimental parameters, calculate the figures for k^H/k^D shown in the alternate columns of Table III. There is seen to be a good measure of agreement between observed and calculated values. Certainly, the fact that the solvent isotope effect results in k^H/k^D values greater than unity rules out the possibility of a proton preequilibration mechanism for the ring opening of the carbonato cobaltic complexes. This is in sharp contrast with the proposal for the phosphato analog,¹⁹ for which a k^H/k^D ratio of less than unity is to be expected,²² and could be as small as 0.3.²³

Acknowledgment. Financial support of this work by the U. S. Atomic Energy Commission through Contract No. AT(30-1)-1578 with the State University of New York at Buffalo is gratefully acknowledged.

(22) E. L. Purlee, *J. Amer. Chem. Soc.*, **81**, 263 (1959).

(23) NOTE ADDED IN PROOF. A value for k_0 of $5 \times 10^{-5} \text{ sec}^{-1}$ is recently reported for the $(en)_2$ complex in 1.0 M NaClO₄ at 25°: D. J. Francis and R. B. Jordan, *ibid.*, **91**, 6626 (1969). The agreement with our rather approximate value of 10^{-4} sec^{-1} for this constant under very different ionic strength conditions is as good as can be expected.

The Reaction of Amines with Haloalkanes. II. The Dissolution of Copper in *n*-Butylamine–Carbon Tetrachloride Solutions

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Contribution from the John Harrison Laboratory of Chemistry and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104. Received November 25, 1969

Abstract: Despite earlier reports that copper metal initiates reaction between amines and haloalkanes at room temperature, it has been found that the metal is inactive in the absence of oxygen. A kinetic study has been made of the dissolution of copper in CCl₄-*n*-butylamine solutions saturated with O₂ at a total pressure of 1 atm. Similarities to the dissolution of copper in aqueous solutions of ammonia or amines under O₂ at high pressure have been found, but in the system studied here the rate-determining step is the formation of copper(I) chloride on the surface of the metal. A mechanism involving a charge-transfer complex formed between amine and CCl₄ is proposed to account for the results obtained.

Rapid reaction of amines with haloalkanes can be initiated by ultraviolet light, by daylight at certain concentrations, or by Cu (I) or Fe (II) salts.¹ It has also been reported²⁻⁵ that copper metal initiates reaction at room temperature. The experiments on which those reports were based were preliminary in nature and did not reveal the cause of the great effect reported for the copper metal. The problem was complicated at that time by the lack of recognition of the existence of the several other initiatory processes and by the lack of in-

formation on the course of the reactions following initiation. With better understanding of those matters now on hand,¹ it has been possible to study the action of the copper metal with greater certainty.

We have found that copper metal is rendered inactive by exclusion of oxygen and we have made a study of the dissolution of the copper in the presence of oxygen in solutions of *n*-butylamine and carbon tetrachloride. The results are in accord with a mechanism in which the oxygen forms activated sites on the metal surface, followed by adsorption of amine at those sites, and, finally, by reaction of metal, amine, and carbon tetrachloride at those activated sites. The reaction probably involves charge-transfer complex formation and generates trichloromethyl radicals.

Experimental Section

Materials. The *n*-butylamine and carbon tetrachloride were prepared as before.¹ Reagent-grade methanol (Baker) was dried

(1) For a recent study of the photochemical and metal-ion initiations and for references to other studies of the reaction, see W. J. Lautenberger, E. N. Jones, and J. G. Miller, *J. Amer. Chem. Soc.*, **90**, 1110 (1968).

(2) G. J. Beichl, Ph.D. Dissertation, University of Pennsylvania, 1953; G. J. Beichl, J. E. Colwell, and J. G. Miller, *Chem. Ind. (London)*, 203 (1960).

(3) N. H. Cromwell, P. W. Foster, and M. M. Wheeler, *ibid.*, 228 (1959).

(4) M. Pesez and J. Bartos, *Bull. Soc. Chim. Fr.*, 1122 (1963).

(5) G. Heublein, *J. Prakt. Chem.*, **31**, 76 (1966).